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(54)【発明の名称】　リン酸基含有固体高分子電解質（複合）膜及びその製造方法

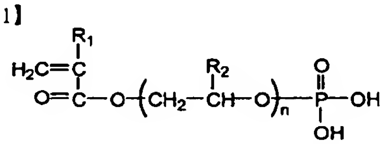
(57)【要約】
【課題】　燃料電池等に使用するのに十分な高導電性を有するとともに、耐熱性及び耐薬品性に優れた固体高分子電解質（複合）膜、及びその製造方法を提供する。
【解決手段】　リン酸基／スルホン酸基含有樹脂と補強シートとからなるプロトン伝導性を有する固体高分子電解質複合膜は、分子内に1個以上のリン酸基及び1個以上のエチレン性不飽和結合を有するリン酸基含有不飽和単量体と、分子内に1個以上のスルホン酸基及び1個以上のエチレン性不飽和結合を有するスルホン酸基含有不飽和単量体とを含有する組成物を、補強シートに含浸させるか塗布した後、前記リン酸基含有不飽和単量体と前記スルホン酸基含有不飽和単量体とを共重合することにより製造することができる。

【特許請求の範囲】

【請求項１】　分子内に１個以上のリン酸基と１個以上のエチレン性不飽和結合とを有するリン酸基含有不飽和単量体と、分子内に１個以上のスルホン酸基及び１個以上のエチレン性不飽和結合を有するスルホン酸基含有不飽和単量体とを共重合体してなるリン酸基／スルホン酸基含有樹脂からなることを特徴とする固体高分子電解質膜。

【請求項２】　請求項１に記載の固体高分子電解質膜において、前記リン酸基含有不飽和単量体は、下記一般式（A）：

【化1】


…(A)

（ただしR_1は水素又はアルキル基であり、R_2は水素又は置換又は無置換のアルキル基であり、nは1～6の整数である。）により表されることを特徴とする固体高分子電解質膜。

【請求項３】　請求項２に記載の固体高分子電解質膜において、R_1はH又はCH_3であり、R_2はH、CH_3又はCH_2Clであることを特徴とする固体高分子電解質膜。

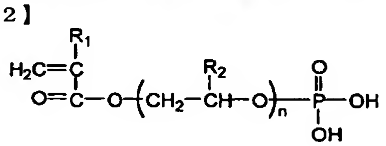
【請求項４】　請求項１～３のいずれかに記載の固体高分子電解質膜において、前記スルホン酸基含有不飽和単量体がp-スチレンスルホン酸であることを特徴とする固体高分子電解質膜。

【請求項５】　リン酸基／スルホン酸基含有樹脂からなるプロトン伝導性を有する固体高分子電解質膜を製造する方法であって、分子内に１個以上のリン酸基と１個以上のエチレン性不飽和結合とを有するリン酸基含有不飽和単量体と、分子内に１個以上のスルホン酸基及び１個以上のエチレン性不飽和結合を有するスルホン酸基含有不飽和単量体との混合物をキャスティングした後、共重合することを特徴とする方法。

【請求項６】　請求項５に記載の方法において、前記リン酸基含有不飽和単量体と前記スルホン酸基含有不飽和単量体との混合物に光重合開始剤を添加し、得られた組成物を成形ダイ上にキャスティングした後、少なくとも一方の面を紫外線透過性板で覆い、紫外線を照射することにより前記リン酸基含有不飽和単量体と前記スルホン酸基含有不飽和単量体とを共重合することを特徴とする方法。

【請求項７】　請求項５又は６に記載の方法において、前記リン酸基含有不飽和単量体は、下記一般式（A）：

【化２】


…(A)

（ただしR_1は水素又はアルキル基であり、R_2は水素又は置換又は無置換のアルキル基であり、nは1～6の整数である。）により表されることを特徴とする方法。

【請求項８】　請求項７に記載の方法において、R_1はH又はCH_3であり、R_2はH、CH_3又はCH_2Clであることを特徴とする方法。

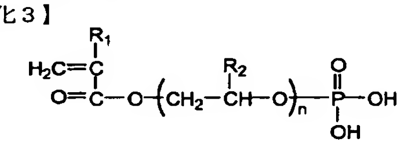
【請求項９】　請求項５～８のいずれかに記載の方法において、前記スルホン酸基含有不飽和単量体がp-スチレンスルホン酸であることを特徴とする方法。

【請求項10】　リン酸基含有樹脂と補強シートとからなることを特徴とするプロトン伝導性を有する固体高分子電解質複合膜。

【請求項11】　請求項10に記載の固体高分子電解質複合膜において、前記リン酸基含有樹脂が、分子内に１個以上のリン酸基と１個以上のエチレン性不飽和結合とを有するリン酸基含有不飽和単量体を重合してなるプロトン伝導性固体高分子であることを特徴とする固体高分子電解質複合膜。

【請求項12】　請求項10又は11に記載の固体高分子電解質複合膜において、前記リン酸基含有不飽和単量体は、下記一般式（A）：

【化３】


…(A)

（ただしR_1は水素又はアルキル基であり、R_2は水素又は置換又は無置換のアルキル基であり、nは1～6の整数である。）により表されることを特徴とする固体高分子電解質複合膜。

【請求項13】　請求項12に記載の固体高分子電解質複合膜において、R_1はH又はCH_3であり、R_2はH、CH_3又はCH_2Clであることを特徴とする固体高分子電解質複合膜。

【請求項14】　請求項10～13のいずれかに記載の固体高分子電解質複合膜において、前記補強シートが無機質又は有機質の繊維からなるシートであることを特徴とする固体高分子電解質複合膜。

【請求項15】　請求項14に記載の固体高分子電解質複合膜において、前記補強シートが織布、不織布又は紙であることを特徴とする固体高分子電解質複合膜。

【請求項16】　請求項10～13のいずれかに記載の固体高分子電解質複合膜において、前記補強シートが樹脂フィルムであることを特徴とする固体高分子電解質複合膜。

【請求項17】　請求項16に記載の固体高分子電解質複合膜において、前記樹脂フィルムが微多孔性であることを特徴とする固体高分子電解質複合膜。

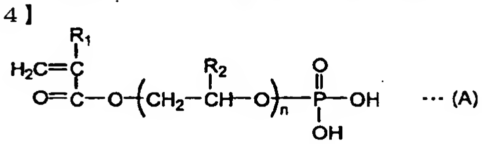
【請求項18】　リン酸基含有樹脂と補強シートとからなるプロトン伝導性を有する固体高分子電解質複合膜を製造する方法であって、分子内に１個以上のリン酸基及び１個以上のエチレン性不飽和結合を有するリン酸基含有

不飽和単量体を、補強シートに含浸させるか塗布した後、前記リン酸基含有不飽和単量体を重合することを特徴とする方法。

【請求項19】　請求項18に記載の方法において、前記リン酸基含有不飽和単量体及び光重合開始剤を含有する組成物を補強シートに含浸させるか塗布した後、前記補強シートを紫外線透過性の支持基板に挟み、紫外線を照射することにより前記リン酸基含有不飽和単量体を重合することを特徴とする方法。

【請求項20】　請求項18又は19に記載の方法において、前記リン酸基含有不飽和単量体は、下記一般式（A）：

【化４】



（ただしR_1は水素又はアルキル基であり、R_2は水素又は置換又は無置換のアルキル基であり、nは1～6の整数である。）により表されることを特徴とする方法。

【請求項21】　請求項20に記載の方法において、R_1はH又はCH_3であり、R_2はH、CH_3又はCH_2Clであることを特徴とする方法。

【請求項22】　請求項18～21のいずれかに記載の方法において、前記補強シートが無機質又は有機質の繊維からなるシートであることを特徴とする方法。

【請求項23】　請求項22に記載の方法において、前記補強シートが織布、不織布又は紙であることを特徴とする方法。

【請求項24】　請求項18～21のいずれかに記載の方法において、前記補強シートが樹脂フィルムであることを特徴とする方法。

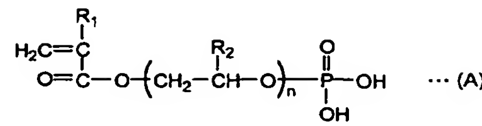
【請求項25】　請求項24に記載の方法において、前記樹脂フィルムが微多孔性であることを特徴とする方法。

【請求項26】　リン酸基／スルホン酸基含有樹脂と補強シートとからなることを特徴とするプロトン伝導性を有する固体高分子電解質複合膜。

【請求項27】　請求項26に記載の固体高分子電解質複合膜において、前記リン酸基／スルホン酸基含有樹脂は、分子内に１個以上のリン酸基と１個以上のエチレン性不飽和結合とを有するリン酸基含有不飽和単量体と、分子内に１個以上のスルホン酸基及び１個以上のエチレン性不飽和結合を有するスルホン酸基含有不飽和単量体との共重合体であることを特徴とする固体高分子電解質複合膜。

【請求項28】　請求項26又は27に記載の固体高分子電解質複合膜において、前記リン酸基含有不飽和単量体は、下記一般式（A）：

【化５】



（ただしR_1は水素又はアルキル基であり、R_2は水素又は置換又は無置換のアルキル基であり、nは1～6の整数である。）により表されることを特徴とする固体高分子電解質複合膜。

【請求項29】　請求項28に記載の固体高分子電解質複合膜において、R_1はH又はCH_3であり、R_2はH、CH_3又はCH_2Clであることを特徴とする固体高分子電解質複合膜。

【請求項30】　請求項26～29のいずれかに記載の固体高分子電解質複合膜において、前記スルホン酸基含有不飽和単量体がp-スチレンスルホン酸であることを特徴とする固体高分子電解質複合膜。

【請求項31】　請求項26～30のいずれかに記載の固体高分子電解質複合膜において、前記補強シートが無機質又は有機質の繊維からなるシートであることを特徴とする固体高分子電解質複合膜。

【請求項32】　請求項31に記載の固体高分子電解質複合膜において、前記補強シートが織布、不織布又は紙であることを特徴とする固体高分子電解質複合膜。

【請求項33】　請求項26～30のいずれかに記載の固体高分子電解質複合膜において、前記補強シートが樹脂フィルムであることを特徴とする固体高分子電解質複合膜。

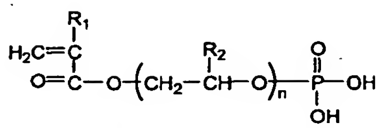
【請求項34】　請求項33に記載の固体高分子電解質複合膜において、前記樹脂フィルムが微多孔性であることを特徴とする固体高分子電解質複合膜。

【請求項35】　リン酸基／スルホン酸基含有樹脂と補強シートとからなるプロトン伝導性を有する固体高分子電解質複合膜を製造する方法であって、分子内に１個以上のリン酸基及び１個以上のエチレン性不飽和結合を有するリン酸基含有不飽和単量体と、分子内に１個以上のスルホン酸基及び１個以上のエチレン性不飽和結合を有するスルホン酸基含有不飽和単量体とを含有する組成物を、補強シートに含浸させるか塗布した後、前記リン酸基含有不飽和単量体と前記スルホン酸基含有不飽和単量体とを共重合することを特徴とする方法。

【請求項36】　請求項35に記載の方法において、前記リン酸基含有不飽和単量体、前記スルホン酸基含有不飽和単量体及び光重合開始剤を含有する組成物を補強シートに含浸させるか塗布した後、前記補強シートを紫外線透過性の支持基板に挟み、紫外線を照射することにより前記リン酸基含有不飽和単量体と前記スルホン酸基含有不飽和単量体とを共重合することを特徴とする方法。

【請求項37】　請求項35又は36に記載の方法において、前記リン酸基含有不飽和単量体は、下記一般式（A）：

【化６】


… (A)

（ただしR_1は水素又はアルキル基であり、R_2は水素又は置換又は無置換のアルキル基であり、nは1～6の整数である。）により表されることを特徴とする方法。

【請求項38】　請求項37に記載の方法において、R_1はH又はCH_3であり、R_2はH、CH_3又はCH_2Clであることを特徴とする方法。

【請求項39】　請求項35～38のいずれかに記載の方法において、前記スルホン酸基含有不飽和単量体がp-スチレンスルホン酸であることを特徴とする方法。

【請求項40】　請求項35～39のいずれかに記載の方法において、前記補強シートが無機質又は有機質の繊維からなるシートであることを特徴とする方法。

【請求項41】　請求項40に記載の方法において、前記補強シートが織布、不織布又は紙であることを特徴とする方法。

【請求項42】　請求項35～39のいずれかに記載の方法において、前記補強シートが樹脂フィルムであることを特徴とする方法。

【請求項43】　請求項42に記載の方法において、前記樹脂フィルムが微多孔性であることを特徴とする方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、一次電池、二次電池、燃料電池等の電解質膜、表示素子、各種センサー、信号伝達媒体、固体コンデンサー、イオン交換膜等に好適な固体高分子電解質（複合）膜及びその製造方法に関し、特に有機溶媒を用いることなく、耐熱性、耐薬品性及び寸法安定性に優れ、広い温度範囲及び湿度範囲にわたり高いプロトン伝導性を示す固体高分子電解質（複合）膜及びその製造方法に関する。

【０００２】

【従来の技術】固体高分子電解質材料として、いわゆる陽イオン交換樹脂に属するポリマー、例えば、ポリスチレンスルホン酸、ポリビニルスルホン酸、パーフルオロスルホン酸ポリマー、パーフルオロカルボン酸ポリマー [Polymer Preprints. Japan Vol. 42. No. 7. pp. 2490～2492 (1993). Polymer Preprints. Japan Vol. 43. No. 3. pp. 735～736 (1994). Polymer Preprints. Japan Vol. 42. No. 3. pp.730 (1993)] 等が報告されている。

【０００３】特に側鎖にスルホン酸基を有する固体高分子材料は、特定のイオンと強固に結合したり、陽イオン又は陰イオンを選択的に透過する性質を有しているので、粒子状、繊維状又は膜状に成形して、電気透析膜、拡散透析膜、電池隔膜等、各種の用途に利用されている。中でも、Nafion（DuPont社製）の商標で知られるパーフルオロ骨格の側鎖にスルホン酸基を有するフッ素系高分子電解質膜は耐熱性及び耐薬品性に優れ、苛酷な条件下での使用に耐える電解質膜として実用化されている。しかし、上記のようなフッ素系電解質膜は製造が困難であるために、非常に高価であるという問題を抱えている。

【０００４】一方、ポリベンズイミダゾール等の炭化水素骨格を有する耐熱性樹脂にアルキルスルホン酸基又はアルキルリン酸基を導入した固体高分子電解質も報告されている（特開平9-87570号、特開平9-110982号）。この固体高分子電解質は、含水状態において100℃の高温下でも高い導電性（10^{-4}～10^{-2} Scm^{-1}）を示すとともに、優れた耐熱性（重量減少開始温度：250℃以上）を有するが、無水状態では導電性を示さない上、キャストフィルムを作成する際にジメチルアセトアミド等の有害な溶媒を使用しなければならない。またポリベンズイミダゾール等の耐熱性樹脂が非常に高価であるため、コストパフォーマンスの点から自動車用燃料電池等の汎用材料としては問題が多い。またポリベンズイミダゾール骨格に限らず、一般に炭化水素骨格を有する樹脂は耐酸化劣化性に劣るので、耐久性に問題があると報告されている（特開2000-11755号）。さらにより高い導電性を有する固体高分子電解質が望まれている。

【０００５】

【発明が解決しようとする課題】従って本発明の目的は、燃料電池等に使用するのに十分な高導電性を有するとともに、耐熱性及び耐薬品性に優れた固体高分子電解質膜、及びその製造方法を提供することである。

【０００６】本発明のもう１つの目的は、燃料電池に使用するのに十分な高導電性を有するとともに、機械的強度及び耐熱性、耐薬品性、寸法安定性等の耐久性に優れた固体高分子電解質複合膜、及びその製造方法を提供することである。

【０００７】

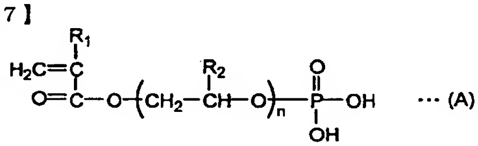
【課題を解決するための手段】上記目的に鑑み鋭意研究の結果、本発明者等は、分子内に１個以上のリン酸基及び１個以上のエチレン性不飽和結合を有するリン酸基含有不飽和単量体と、分子内に１個以上のスルホン酸基及び１個以上のエチレン性不飽和結合を有するスルホン酸基含有不飽和単量体との共重合体からなる固体高分子電解質膜は、導電性が著しく高く、導電性の温度依存性が低く、耐熱性及び耐薬品性に優れていることを発見した。本発明者等はまた、リン酸基含有不飽和単量体（又はリン酸基含有不飽和単量体及びスルホン酸基含有不飽和単量体）及び重合開始剤を含有する組成物を補強シートに含浸させるか塗布した後、重合させることにより、有機溶媒を用いることなく、広い温度範囲及び湿度範囲にわたり高いプロトン伝導性を示す、機械的強度及び耐久性に優れた固体高分子電解質複合膜が得られることを発見した。本発明はかかる発明に基づき完成したもので

ある。

【０００８】すなわち、本発明の固体高分子電解質膜は、分子内に１個以上のリン酸基と１個以上のエチレン性不飽和結合とを有するリン酸基含有不飽和単量体と、分子内に１個以上のスルホン酸基及び１個以上のエチレン性不飽和結合を有するスルホン酸基含有不飽和単量体とを共重合体してなるリン酸基／スルホン酸基含有樹脂からなることを特徴とする。

【０００９】リン酸基含有不飽和単量体としては、下記一般式(A)：

【化７】



(ただしR_1は水素又はアルキル基であり、R_2は水素又は置換又は無置換のアルキル基であり、nは1～6の整数である。) により表されるものが好ましい。R_1はH又はCH_3であり、R_2はH、CH_3又はCH_2Clであるのが好ましい。

【００１０】スルホン酸基含有不飽和単量体はp-スチレンスルホン酸であるのが好ましい。

【００１１】リン酸基／スルホン酸基含有樹脂からなるプロトン伝導性を有する固体高分子電解質膜を製造する方法は、分子内に１個以上のリン酸基と１個以上のエチレン性不飽和結合とを有するリン酸基含有不飽和単量体と、分子内に１個以上のスルホン酸基及び１個以上のエチレン性不飽和結合を有するスルホン酸基含有不飽和単量体との混合物をキャスティングした後、共重合することを特徴とする。

【００１２】リン酸基含有不飽和単量体とスルホン酸基含有不飽和単量体との混合物に光重合開始剤を添加し、得られた組成物を成形ダイ上にキャスティングした後、少なくとも一方の面を紫外線透過性板で覆い、紫外線を照射することによりリン酸基含有不飽和単量体とスルホン酸基含有不飽和単量体とを共重合するのが好ましい。

【００１３】本発明のプロトン伝導性を有する第一の固体高分子電解質複合膜は、リン酸基含有樹脂と補強シートとからなることを特徴とする。リン酸基含有樹脂は、分子内に１個以上のリン酸基と１個以上のエチレン性不飽和結合とを有するリン酸基含有不飽和単量体を重合してなるプロトン伝導性固体高分子であるのが好ましい。補強シートは無機質又は有機質の繊維からなるシートであるのが好ましい。また補強シートは織布、不織布、紙又は樹脂フィルムであるのが好ましい。樹脂フィルムは微多孔性であるのが好ましい。

【００１４】リン酸基含有樹脂と補強シートとからなるプロトン伝導性を有する第一の固体高分子電解質複合膜を製造する本発明の方法は、分子内に１個以上のリン酸基及び１個以上のエチレン性不飽和結合を有するリン酸基含有不飽和単量体を、補強シートに含浸させるか塗布した後、リン酸基含有不飽和単量体を重合することを特徴とする。

【００１５】上記方法においては、リン酸基含有不飽和単量体及び光重合開始剤を含有する組成物を補強シートに含浸させるか塗布した後、補強シートを紫外線透過性の支持基板に挟み、紫外線を照射することにより、リン酸基含有不飽和単量体を重合するのが好ましい。

【００１６】本発明のプロトン伝導性を有する第二の固体高分子電解質複合膜は、リン酸基／スルホン酸基含有樹脂と補強シートとからなることを特徴とする。リン酸基／スルホン酸基含有樹脂は、分子内に１個以上のリン酸基と１個以上のエチレン性不飽和結合とを有するリン酸基含有不飽和単量体と、分子内に１個以上のスルホン酸基及び１個以上のエチレン性不飽和結合を有するスルホン酸基含有不飽和単量体との共重合体であるのが好ましい。

【００１７】リン酸基／スルホン酸基含有樹脂と補強シートとからなるプロトン伝導性を有する第二の固体高分子電解質複合膜を製造する方法は、分子内に１個以上のリン酸基及び１個以上のエチレン性不飽和結合を有するリン酸基含有不飽和単量体と、分子内に１個以上のスルホン酸基及び１個以上のエチレン性不飽和結合を有するスルホン酸基含有不飽和単量体とを含有する組成物を、補強シートに含浸させるか塗布した後、リン酸基含有不飽和単量体とスルホン酸基含有不飽和単量体とを共重合することを特徴とする。

【００１８】上記方法においては、リン酸基含有不飽和単量体、スルホン酸基含有不飽和単量体及び光重合開始剤を含有する組成物を補強シートに含浸させるか塗布した後、補強シートを紫外線透過性の支持基板に挟み、紫外線を照射することにより、リン酸基含有不飽和単量体とスルホン酸基含有不飽和単量体とを共重合するのが好ましい。

【００１９】本発明の第一及び第二の固体高分子電解質複合膜はいずれも、含水状態において30～80℃の温度範囲で、10^{-5} ～10^{-2} Scm^{-1} の範囲の高い導電性を示すとともに、重量減少開始温度が200℃以上という優れた耐熱性を有し、30～100℃の範囲において伸縮、反り、層間剥離等の外形の変化を起こさず、優れた寸法安定性を示す。特にリン酸基／スルホン酸基含有樹脂を含有する固体高分子電解質複合膜は、導電性の温度依存性が顕著に低く、30～80℃の温度範囲で10^{-3} ～10^{-2} Scm^{-1} の範囲の高い導電性を示す。

【００２０】また常法ではプロトン伝導性高分子電解質膜を調製するに当たって、予め調製しておいた高分子電解質を有機溶剤に溶解してキャスト製膜するところ、本発明の製造方法では単量体組成物に紫外線を照射して重合又は共重合させるので、有機溶剤を取扱う繁雑さから解放される。

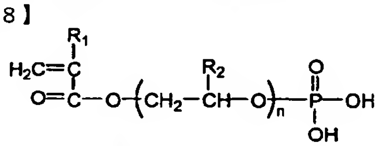
【００２１】

【発明の実施の形態】以下、本発明のリン酸基含有樹脂又はリン酸基／スルホン酸基含有樹脂を含有するプロトン伝導性固体高分子電解質（複合）膜及びそれらの製造方法について詳細に説明する。

[I] リン酸基含有樹脂及びリン酸基／スルホン酸基含有樹脂

本発明に用いるリン酸基含有樹脂及びリン酸基／スルホン酸基含有樹脂は、下記一般式(A)：

【化８】


… (A)

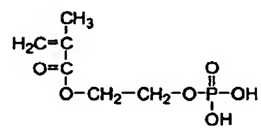
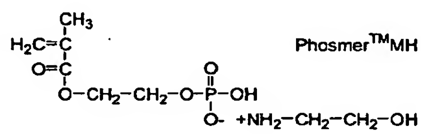
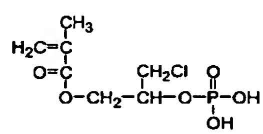
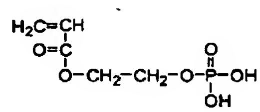
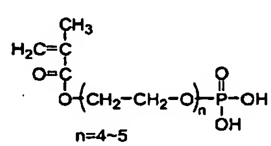
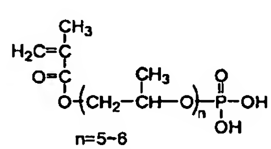
（ただしR_1は水素又はアルキル基であり、R_2は水素又は置換又は無置換のアルキル基であり、nは1～6の整数である。）により表されるリン酸基含有不飽和単量体を必須成分として重合又は共重合したものである。R_1はH又はCH_3であり、R_2はH、CH_3又はCH_2Clであるのが好ましい。上記リン酸基含有不飽和単量体を、これと共重合しうる他の不飽和単量体と共重合してもよい。

【００２２】(1) リン酸基含有不飽和単量体

一般式(A)により表されるリン酸基含有不飽和単量体のうち、本発明に好適に使用できる単量体の構造式を表1に示し、これらの単量体の物性を表2に示す。これらの単量体はユニケミカル（株）から商品名Phosmer™として販売されている。ただし、本発明に使用できるリン酸基含有不飽和単量体はこれらに限定されるものではない。

【００２３】

【表１】

名称	構造式	グレード名
アシッド・ホスホオキシエチルメタクリレート		Phosmer™M
メタクロイル・オキシエチルアシッドホスフェート・モノエタノールアミン塩		Phosmer™MH
3-クロロ-2-アシッド・ホスホオキシプロピルメタクリレート		Phosmer™CL
アシッド・ホスホオキシエチルアクリレート		Phosmer™A
アシッド・ホスホオキシポリオキシエチレングリコールモノメタクリレート		Phosmer™PE
アシッド・ホスホオキシポリオキシプロピレングリコールメタクリレート		Phosmer™PP

【００２４】

【表２】

グレード (Phosmer™)		M	MH	CL	A	PE	PP
分子量(g)/リン酸当量(g)		210	271	258.5	196	333	440
比重 (at 20℃)		1.392	1.302	1.453	1.468	1.248	1.157
屈折率 (nd at 20 °C)		1.4562	1.4815	1.4785	1.4664	1.4696	1.4577
粘度 (poise at 20 °C) Brookfield型粘度計 (ロータNo.) により測定		80 (No. 1)	800 (No. 2)	700 (No. 2)	320 (No. 2)	25 (No. 1)	55 (No. 2)
酸化	理論値	533.3	206.6	433.3	571.4	—	—
	実測値	500以下	196	410以下	—	320	255
製品のpH		—	9.4	—	—	—	—
水溶性	(wt % at 20℃)	4.1	4.3	1.3	9.4	—	—
	(wt % at 25℃)	—	—	—	—	4.0	3.2
単量体が可溶な溶媒		有機酸, ケトン, アルコール	2-ヒドロキシエチルメタクリレート, メタノール, エタノール, イソプロピルアルコール, アクリル酸, 酢酸	有機酸, ケトン, アルコール	同左	同左	ベンゼン, トルエン, キシレン

【００２５】一般式(A)のリン酸基含有不飽和単量体は単独で用いてもよいし、２種以上を併用しても良い。

【００２６】(2) 共重合し得る他の不飽和単量体

上記リン酸基含有不飽和単量体と共重合し得る不飽和単量体は次の２群(2-1)、(2-2)に大別できる。

【００２７】(2-1) 酸基を含有する不飽和単量体

酸基を含有する不飽和単量体は、分子内に少なくとも１つの酸基と、少なくとも１つのエチレン性不飽和結合を有する化合物である。酸基としては、スルホン酸基、カルボン酸基等が挙げられる。このうちスルホン酸基含有不飽和単量体が好ましく、リン酸基含有不飽和単量体とスルホン酸基含有不飽和単量体との共重合により、リン酸基／スルホン酸基含有樹脂が得られる。リン酸基／スルホン酸基含有樹脂を含有する固体高分子電解質（複合）膜は一層優れた導電性を有するとともに、導電性の温度依存性が顕著に低い。

【００２８】スルホン酸基含有不飽和単量体の例としては、アリルスルホン酸、メタアリルスルホン酸、ビニルスルホン酸、p-スチレンスルホン酸、（メタ）アクリル酸ブチル-4-スルホン酸、（メタ）アクリロオキシベンゼンスルホン酸、t-ブチルアクリルアミドスルホン酸、2-アクリル-2-アクリルアミド-2-メチルプロパンスルホン酸等が挙げられる。なかでもp-スチレンスルホン酸が好ましい。ただし、アリルスルホン酸、メタアリルスルホン酸は、そのアリル基がdegradative chaintransferを起こすので、使用量を65重量％未満とするのが好ましい。これらのスルホン酸基含有不飽和単量体は単独でもよいし、２種以上を併用しても良い。カルボン酸基含有不飽和単量体の例としては、（メタ）アクリル酸、クロトン酸、マレイン酸、フマル酸、イタコン酸、マレイン酸無水物等が挙げられる。これらのカルボン酸基含有不飽和単量体は単独でもよいし、２種以上を併用しても良い。

【００２９】(2-2) 酸基を含有しない不飽和単量体

(2-1) に記載した以外で、常温で気体でなく、分子内に１個以上のエチレン性不飽和結合を有する不飽和単量体は全てこの不飽和単量体に含まれるが、中でも（メタ）アクリロニトリル、（メタ）アクリル酸エステル類や置換又は無置換のスチレン類が好適である。１分子内に複数個のエチレン性不飽和結合を含有するエチレングリコールジ（メタ）アクリレート、トリメチロールプロパントリ（メタ）アクリレート、ヘキサメチレンジオールジ（メタ）アクリレートやジビニルベンゼン等も、固体高分子電解質（複合）膜の耐薬品性を改良するために使用するのが好ましい。

【００３０】(3) 各不飽和単量体の重量比

リン酸基含有不飽和単量体(1) と他の不飽和単量体(2) との重量比(1)/(2) は100/0～20/80の範囲であるが、好ましくは(1)/(2) = 80/20～50/50である。また他の不飽和単量体(2) の中で、酸基を含有する不飽和単量体(2-1) とそれ以外の不飽和単量体(2-2) の重量比は、プロトン伝導性にプラス効果をもたらす(2-1) が支配的になるように、(2-1)/(2-2) = 100/0～50/50の範囲とするのが好ましい。従って、特に酸基を含有する不飽和単量体(2-1)としてスルホン酸基含有不飽和単量体を使用する場合、リン酸基含有不飽和単量体／スルホン酸基含有不飽和単量体の重量比は100/0～20/80、好ましくは80/20～50/50であり、スルホン酸基含有不飽和単量体／他の

酸基含有不飽和単量体の重量比は100/0～50/50である。

【００３１】[II] 光重合開始剤

本発明で単量体組成物に加える光重合開始剤としては、(1) R-(CO)ₓ-R'（R, R' = 水素又は炭化水素基、x = 2～3）により表される隣接ポリケトン化合物類（例えばジアセチル、ジベンジル等）、(2) R-CO-CHOH-R'（R, R' = 水素又は炭化水素基）により表されるα-カルボニルアルコール類（例えばベンゾイン等）、(3) R-CH(OR")-CO-R'（R, R', R"=炭化水素基）により表されるアシロイン・エーテル類（例えばベンゾインメチルエーテル等）、(4) Ar-CR(OH)-CO-Ar（Ar = アリール基、R = 炭化水素基）により表されるα-置換アシロイン類（例えばα-アルキルベンゾイン等）、及び(5) 多核キノン類（例えば9,10-アンスラキノン等）がある。これらの光重合開始剤は、それぞれ単独で又は併用して使用することができる。

【００３２】光重合開始剤の使用量は、不飽和単量体の合計重量に対して0.5～5重量%の範囲、好ましくは1～3重量%の範囲である。0.5重量%未満だと、所定の紫外線照射時間内に重合又は共重合が完結せず、未反応単量体が残留するので好ましくない。また光重合開始剤の使用量が5重量%超だと、得られる樹脂の重合度が低すぎ、樹脂が着色する傾向にあるので好ましくない。

【００３３】本発明では、光重合開始剤の単量体混合物への溶解を容易にし、不飽和単量体の粘度を下げ、補強シートへの含浸を容易にし、補強シートへの付着量を減少せしめて固体高分子電解質（複合）膜の膜厚を薄くする等の目的で、希釈剤としてメタノール、アセトン等の低沸点溶剤を加えても良い。

【００３４】[III] 補強シート

本発明に使用する補強シートは、下記の３群に大別できる。

(1) 無機質繊維からなるシート

ガラス繊維、アルミナ繊維、ロックウール繊維、スラグ繊維等からなる織布、不織布、紙等が挙げられる。無機質繊維からなるシートの坪量は10～60 mg/cm²、好ましくは10～40 mg/cm²であり、厚さは1～60 μm、好ましくは5～40 μmの範囲である。

【００３５】(2) 有機質繊維からなるシート

ナイロン繊維、ポリエステル繊維、アクリル繊維、アラミド繊維等からなる織布、不織布、紙等が挙げられる。ただし、紫外線照射時に固体高分子電解質（複合）膜の温度が100℃近くまで上昇することもあるので、それに耐えるのに十分な耐熱性を有することが必要である。有機質繊維からなるシートの坪量と厚さは、(1)の場合と同じである。ただし、含浸又は塗布する単量体組成物がスルホン酸基等の強酸基を有する不飽和単量体を含む場合、ナイロン繊維からなる織布、不織布、紙等は、耐酸性が弱いために不適である。

【００３６】(3) 樹脂フィルム

単量体組成物を含浸又は塗布する樹脂フィルムとしては、ポリエチレン樹脂、ポリプロピレン樹脂、ポリ3-メチルペンテン樹脂、ナイロン-6樹脂、ポリエステル樹脂、熱可塑性ポリウレタン樹脂、ポリスルホン樹脂、ポリエーテルスルホン樹脂、ポリエーテルエーテルケトン樹脂、アラミド樹脂、ポリイミド樹脂、フッ素系樹脂等のフィルムが好ましい。樹脂フィルムは微多孔性フィルムでも無孔フィルムでもよいが、単量体組成物の含浸性の観点から、前者が好ましい。ただし、含浸させる単量体組成物がスルホン酸基等の強酸基を有する不飽和単量体を含む場合、ナイロンフィルムは、耐酸性が強くないため、不適である。

【００３７】微多孔性フィルムの場合、微孔の孔径は出来るだけ小さいのが好ましく、特にサブミクロン径であるのが好ましい。また微多孔性フィルム全体の開孔率は出来るだけ大きい方が好ましく、特に40～50%（対表面積）であるのが好ましい。樹脂フィルムの厚さは1～40 μmが好ましく、5～25 μmの範囲がより好ましい。

【００３８】補強シートと単量体組成物の重量比は、補強シートの単量体組成物に対する親和性、換言すれば、単量体組成物の吸収性によって大きく異なるが、一般的に補強シート／単量体組成物の重量比は1/20～1/2の範囲であるのが好ましい。

【００３９】[IV] 固体高分子電解質（複合）膜の製造方法

リン酸基含有不飽和単量体とスルホン酸基含有不飽和単量体からなる固体高分子電解質膜の場合、両不飽和単量体及び光重合開始剤を含有する組成物を成形ダイにキャスティングし、紫外線透過性板で覆った後、紫外線を照射して両不飽和単量体を共重合させることにより、製造することができる。

【００４０】またリン酸基含有不飽和単量体（又はリン酸基含有不飽和単量体及びスルホン酸基含有不飽和単量体）と補強シートからなる固体高分子電解質複合膜の場合、不飽和単量体及び光重合開始剤を含有する組成物を補強シートに含浸させるか塗布した後、補強シートを紫外線透過性の支持基板に挟み、紫外線を照射して不飽和単量体を光重合することにより、製造することができる。

【００４１】不飽和単量体組成物を含浸した補強シートを紫外線照射重合するに当たって、これを挟む２枚の支持基板は紫外線透過率が高いことのみならず、紫外線照射による重合時の昇温に耐える耐熱性を有すること、及び不飽和単量体組成物及びこれを重合して得られる固体高分子電解質と接着せず、剥離性が良好なことが必要である。

【００４２】通常使用するガラス平板は紫外線透過率と耐熱性については非常に良いが、本発明に使用する不飽和単量体の重合又は共重合により得られる固体高分子電解質と密着するので、予めガラス平板の表面にシリコー

ン系又はフッ素系の剥離剤を塗布しておくか、フッ素樹脂系の薄い透明フィルムを貼りつけた上で使用するのが好ましい。

【００４３】ガラス平板以外に、ポリパーフルオロビニルエーテル樹脂（PFA）、ポリフッ化ビニリデン樹脂（PVDF）等のフッ素系樹脂の他、ポリ3-メチルペンテン樹脂、ポリプロピレン樹脂等の紫外線透過率の良い100℃以上の耐熱性を有する樹脂平板を使用することができる。

【００４４】不飽和単量体組成物をキャスティングした後で紫外線透過性板で覆って紫外線照射を行うか、不飽和単量体組成物を含浸させるか塗布した補強シートを２枚の支持基板の間に挟んで紫外線照射を行うに当たって、空気及び余分な不飽和単量体組成物を系外に絞り出す必要がある。例えば補強シートを使用する場合、図１に示すように、２枚の支持基板の間に均等に圧力をかけて、クリップ又はクランプで止めた状態で、水平に保ちながら紫外線照射を行うのが好ましい。光重合時の紫外線照射強度は5～50 mW/cm^2、好ましくは10～25 mW/cm^{2}とする。

【００４５】固体高分子電解質（複合）膜の厚さは300 μm以下、好ましくは10～100 μm、より好ましくは10～30 μmとする。

【００４６】

【実施例】本発明を以下の実施例により更に詳細に説明するが、本発明はこれらに限定されるものではない。

【００４７】実施例１～16、比較例１～４

表３に示す不飽和単量体組成物に希釈剤としてメタノールを添加して粘度を調整した後、不飽和単量体全体を100重量％として、光重合開始剤として２重量％のイルガキュア651（2,2-ジメトキシ-1,2-ジフェニルエタン-1-オン）及び１重量％のイルガキュア500（1-ヒドロキシシクロヘキシルフェニルケトン＋ベンゾフェノン）を溶解した。補強シートとして各種の不織布又は紙を採用し、不飽和単量体組成物を補強シートに含浸させた後、図１及び図２に示すように、シリコーン剥離剤を塗布したガラス平板２枚の間に不飽和単量体組成物含浸補強シート挟んだ。高圧水銀灯（東芝電材（株）製トスキュア400，HC-0411型）を用いて、不飽和単量体組成物含浸補強シートに20 mW/cm^{2}の紫外線を所定時間照射して、不飽和単量体組成物を光重合させ、固体高分子電解質複合膜を作製した。不飽和単量体組成物、補強シートの種類及び坪量、紫外線照射時間、及び複合膜の性状を表3に示す。

【００４８】

【表３】

例 No.		実施例 1			実施例 2			実施例 3	
不飽和単量体組成物 (wt. %)	Phosmer M	50			−			50	
	Phosmer PP	50			95			50	
	PSSA(1)	−			−			−	
	HDDA(2)	−			5			−	
希釈剤 MeOH (wt. %)		0	50	75	0	50	75	50	75
補強材シート	種類	GF 不織布 GHN-30CGL(3)			GF 不織布 GHN-30CGL			GF 不織布 GMC-050E(4)	
	坪量(mg/cm^2)	30			30			50	
照射時間［表＋裏（sec)］		40 + 40			40 + 40			40 + 40	
複合膜	樹脂／補強材シート(10)	9.6	7.5	4.7	8.5	6.1	4.2	7.2	4.0
	平滑性	良好			良好			良好	
	ピンホール	ナシ			ナシ			ナシ	
	厚さ(μm)	170	140	110	160	130	110	170	120
	導電率測定の有無	No			No			Yes	No

【００４９】表３つづき

例 No.		実施例 4		実施例 5	実施例 6
不飽和単量体組成物 (wt. %)	Phosmer M	−		50	−
	Phosmer PP	95		50	95
	PSSA(1)	−		−	−
	HDDA(2)	5		−	5
希釈剤 MeOH (wt. %)		50	75	75	50
補強材シート	種類	GF 不織布 GMC-050E		GF 紙(5)	GF 紙
	坪量(mg/cm²)	50		40	40
照射時間［表＋裏 (sec)］		40 + 40		40 + 40	40 + 40
複合膜	樹脂／補強材シート(10)	6.0	5.0	4.5	5.3
	平滑性	良好		良好	良好
	ピンホール	ナシ		ナシ	ナシ
	厚さ(μm)	160	100	90	87
	導電率測定の有無	Yes	No	No	No

【００５０】表３つづき

例 No.		実施例 7	実施例 8	実施例 9
不飽和単量体組成物 (wt. %)	Phosmer M	50	−	50
	Phosmer PP	50	95	50
	PSSA(1)	−	−	−
	HDDA(2)	−	5	−
希釈剤 MeOH (wt. %)		75	50	75
補強材シート	種類	PAN 紙(6)	PAN 紙	アラミド不織布 XL-1040(7)
	坪量(mg/cm²)	38	38	40
照射時間［表＋裏 (sec)］		40 + 40	40 + 40	120 + 120
複合膜	樹脂／補強材シート(10)	3.8	5.0	13.3
	平滑性	良好	良好	良好
	ピンホール	ナシ	ナシ	ナシ
	厚さ(μm)	75	70	200
	導電率測定の有無	Yes	Yes	Yes

【００５１】表３つづき

例 No.		実施例 10	実施例 11	実施例 12
不飽和単量体組成物 (wt. %)	Phosmer M	−	50	−
	Phosmer PP	95	50	95
	PSSA(1)	−	−	−
	HDDA(2)	5	−	5
希釈剤 MeOH (wt. %)		50	75	50
補強材シート	種類	アラミド不織布 XL-1040	アラミド紙(8)	アラミド紙
	坪量(mg/cm^2)	40	35	35
照射時間〔表＋裏 (sec)〕		120 + 120	120 + 120	120 + 120
複合膜	樹脂／補強材シート(10)	10.1	5.6	4.7
	平滑性	良好	良好	良好
	ピンホール	ナシ	ナシ	ナシ
	厚さ(μm)	190	45	38
	導電率測定の有無	Yes	Yes	Yes

【００５２】表３つづき

例 No.		実施例 13	実施例 14	実施例 15
不飽和単量体組成物 (wt. %)	Phosmer M	50	−	50
	Phosmer PP	50	95	−
	PSSA(1)	−	−	50
	HDDA(2)	−	5	−
希釈剤 MeOH (wt. %)		50	50	70
補強材シート	種類	ハイポア 6022(9)	ハイポア 6022	GF 不織布 GHN-30CGL
	坪量(mg/cm^2)	25	25	30
照射時間〔表＋裏 (sec)〕		40 + 40	40 + 40	60 + 60
複合膜	樹脂／補強材シート(10)	3.1	2.7	2.3
	平滑性	良好	良好	良好
	ピンホール	ナシ	ナシ	ナシ
	厚さ(μm)	37	20	104
	導電率測定の有無	No	No	Yes

【００５３】表３つづき

例 No.		実施例 16	比較例 1	比較例 2
不飽和単量体組成物 (wt. %)	Phosmer M	50	50	−
	Phosmer PP	−	50	95
	PSSA(1)	50	−	−
	HDDA(2)	−	−	5
希釈剤 MeOH (wt. %)		70	50	50
補強材シート	種類	ナイロンネット	−	−
	坪量(mg/cm^2)	50	−	−
照射時間〔表＋裏 (sec)〕		60 + 60	40 + 40	40 + 40
複合膜	樹脂／補強材シート(10)	0.8	−	−
	平滑性	良好	良好	良好
	ピンホール	ナシ	ナシ	ナシ
	厚さ(μm)	約 100	約 30	約 20
	導電率測定の有無	Yes	No	No

【００５４】表３つづき

例 No.		比較例 3	比較例 4
不飽和単量体組成物 (wt. %)	Phosmer M	−	−
	Phosmer PP	−	−
	PSSA(1)	100	100
	HDDA(2)	−	−
希釈剤 MeOH (wt. %)		82	82
補強材シート	種類	GF 不織布 GHN-30CGL	ナイロンネット
	坪量(mg/cm^2)	30	50
照射時間〔表＋裏 (sec)〕		60 + 60	60 + 60
複合膜	樹脂／補強材シート(10)	1.4	0.3
	平滑性	良好	良好
	ピンホール	ナシ	ナシ
	厚さ(μm)	52	100
	導電率測定の有無	Yes	Yes

注：(1) PSSA： p-スチレンスルホン酸
(2) HDDA： ヘキサメチレンジオールジアクリレート
(3) GF（グラスファイバー）不織布 GHN-30CGL（王子製紙(株)製の市販品）
(4) GF（グラスファイバー）不織布 GMC-050E（王子製紙(株)製の市販品）
(5) GF（グラスファイバー）紙（阿波製紙(株)製の試作品）
(6) PAN（ポリアクリロニトリル）紙（阿波製紙(株)製の試作品）
(7) アラミド不織布 XL-1040（日本バイリーン(株)製の試作品）

(8) アラミド紙（阿波製紙(株)製の試作品）
(9) PE(ポリエチレン)微多孔フィルム　ハイポア™ 6022（旭化成工業(株)製）
(10) 樹脂／補強材シートの重量比。

【００５５】実施例及び比較例の代表的な固体高分子電解質複合膜について、相対湿度90%及び温度範囲30～80℃で導電率を測定した。結果を図３～図５に示す。

【００５６】図３～図５に示す結果から、本発明の方法に従えば、いずれの補強シートを用いても、表面が平滑でピンホールのない固体高分子電解質複合膜を作ることができることが分かる。なお希釈剤を使用することにより、補強シートに付着する樹脂量を数分の１以下にすることができた。実施例の固体高分子電解質複合膜の厚さは20～200 μmの範囲であるが、補強シートの坪量、補強シートと不飽和単量体組成物との親和性、樹脂の付着割合、換言すれば単量体組成物の付着量とそれを搾り出す圧力を適宜調整することにより、所望の厚さとすることができる。

【００５７】図３～図５に示す結果から、本発明の固体高分子電解質複合膜の導電率は10^{-5}～10^{-2} Scm^{-1}のオーダーであり、リン酸基を官能基とする高分子電解質としては良好な水準にあることが分かる。特にリン酸基含有不飽和単量体とp-スチレンスルホン酸との共重合体からなるリン酸基／スルホン酸基含有樹脂を含有する固体高分子電解質複合膜（実施例15及び16）は、導電性の温度依存性が著しく低く、30～80℃の温度範囲で10^{-3}～10^{-2} Scm^{-1}と高い導電性を示した。これに対して比較例３及び４の固体高分子電解質複合膜はp-スチレンスルホン酸の単独重合体を用いているため、実施例15及び16の固体高分子電解質複合膜に比べて導電性が低く、導電性の温度依存性が高い。

【００５８】以上の実施例では補強シートを有する固体高分子電解質複合膜の実験結果を示したが、補強シートを有さない固体高分子電解質膜も同じ電解質特性を有することは明らかである。従って高い機械的強度が要求されない用途には、補強シートを有さない固体高分子電解質膜を好適に使用することができる。

【００５９】

【発明の効果】以上詳述した通り、リン酸基含有不飽和単量体及びスルホン酸基含有不飽和単量体を含む組成物をキャスティングした後で紫外線照射等により共重合させるか、リン酸基含有不飽和単量体（又はリン酸基含有不飽和単量体及びスルホン酸基含有不飽和単量体）を含む組成物を補強シートに含浸又は塗布した後、紫外線照射等により重合又は共重合することにより、有機溶媒を排出することなく、広い温度範囲及び湿度範囲にわたり高いプロトン伝導性を示す固体高分子電解質（複合）膜を得ることができる。特に補強シートを用いた固体高分子電解質複合膜の場合、耐熱性、耐薬品性及び寸法安定性に優れているという利点を有する。

【００６０】またリン酸基含有不飽和単量体とスルホン酸基含有不飽和単量体との共重合体からなるリン酸基／スルホン酸基含有樹脂を含有する固体高分子電解質（複合）膜は、導電性が一層高く、導電性の温度依存性が低い。このような特徴を有する本発明の固体高分子電解質（複合）膜は、一次電池、二次電池、燃料電池等の固体電解質膜、表示素子、各種センサー、信号伝達媒体、固体コンデンサー、イオン交換膜等に好適である。

【図面の簡単な説明】

【図１】　ガラス平板２枚の間に固体高分子電解質複合膜を挟んだ状態を示す部分断面側面図である。

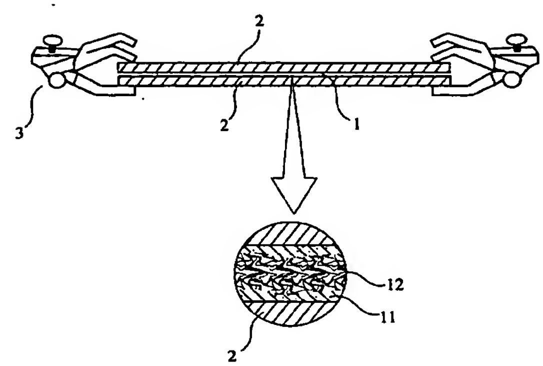
【図２】　ガラス平板２枚の間に固体高分子電解質複合膜を挟んだ状態を示す平面図である。

【図３】　(a)は実施例３及び４の固体高分子電解質複合膜について、温度T(℃)と導電率log（σ/Scm^{-1}）との関係を示すグラフであり、(b)は実施例７及び８の固体高分子電解質複合膜について、温度T(℃)と導電率log（σ/Scm^{-1}）との関係を示すグラフである。

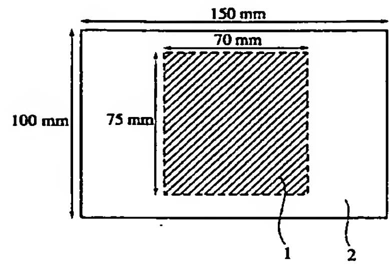
【図４】　(a)は実施例９及び10の固体高分子電解質複合膜について、温度T(℃)と導電率log（σ/Scm^{-1}）との関係を示すグラフであり、(b)は実施例11及び12の固体高分子電解質複合膜について、温度T(℃)と導電率log（σ/Scm^{-1}）との関係を示すグラフである。

【図５】　(a)は実施例15及び比較例３の固体高分子電解質複合膜について、温度T(℃)と導電率log（σ/Scm^{-1}）との関係を示すグラフであり、(b)は実施例16及び比較例４の固体高分子電解質複合膜について、温度T(℃)と導電率log（σ/Scm^{-1}）との関係を示すグラフである。

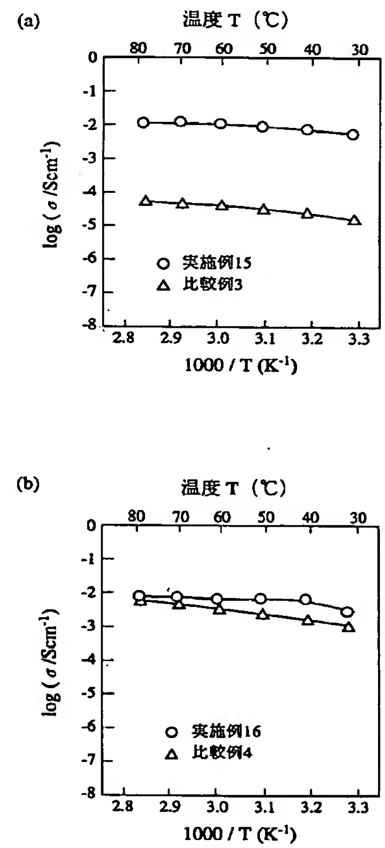
【図１】


2
3
2
1
12
11
2

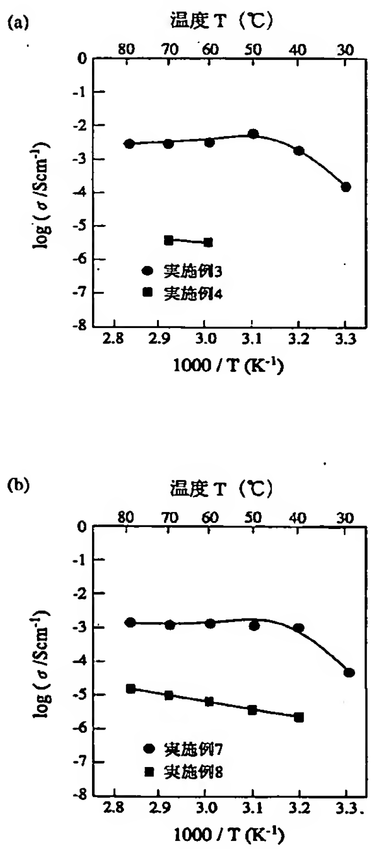
【図２】


150 mm
70 mm
100 mm
75 mm
1
2

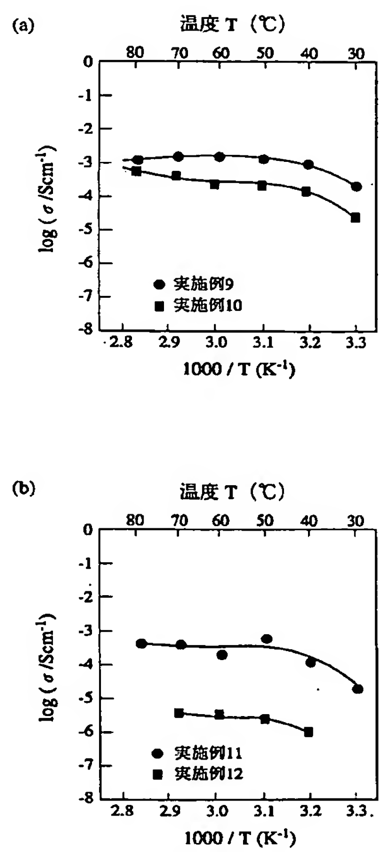
【図５】


(a)
温度 T （℃）
log (σ /Scm-1)
1000 / T (K-1)
○ 実施例15
△ 比較例3
(b)
温度 T （℃）
log (σ /Scm-1)
1000 / T (K-1)
○ 実施例16
△ 比較例4

【図３】


(a)
温度 T （℃）
log (σ /Scm-1)
1000 / T (K-1)
● 実施例3
■ 実施例4
(b)
温度 T （℃）
log (σ /Scm-1)
1000 / T (K-1)
● 実施例7
■ 実施例8

【図４】


(a)
温度 T （℃）
log (σ /Scm-1)
1000 / T (K-1)
● 実施例9
■ 実施例10
(b)
温度 T （℃）
log (σ /Scm-1)
1000 / T (K-1)
● 実施例11
■ 実施例12

フロントページの続き

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ＨＯ１Ｍ 8/02		ＨＯ１Ｍ 8/02	Ｐ
8/10		8/10	

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4J027 AC02 AC06 AC09 BA05 CB10 CC05
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RIKUKAWA MASAHIRO

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(54) SOLID MACROMOLECULAR ELECTROLYTE (COMPOSITE) FILM CONTAINING PHOSPHORIC ACID GROUP AND METHOD FOR MANUFACTURING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To provide solid macromolecular electrolyte (compound) film having sufficiently high conductivity for usages such as a fuel cell and superior in heat resistance and chemical resistance, and a method for manufacturing the same.
SOLUTION: Solid macro molecular electrolyte composite film having proton conductivity composed of resin containing phosphoric acid group/sulfonic group and reinforcement sheet is manufactured by copolymerizing unsaturated monomer containing phosphoric acid group and unsaturated monomer containing sulfonic acid group after impregnating or applying composition containing unsaturated monomer containing phosphoric acid group including one or more phosphoric acid and one or more ethylene unsaturated bond in the molecule and unsaturated monomer containing sulfonic acid group including one or more sulfonic acid and one or more ethylene unsaturated bond in the molecule to the reinforcement sheet.

LEGAL STATUS
[Date of request for examination]
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[Date of registration]
[Number of appeal against examiner's decision of

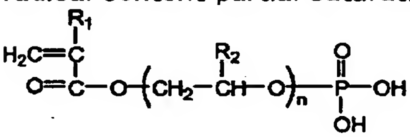
rejection]

[Date of requesting appeal against examiner's decision of rejection]

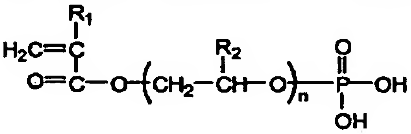
[Date of extinction of right]

CLAIMS

[Claim(s)]
[Claim 1] Solid-state polyelectrolyte film characterized by consisting of a phosphoric-acid radical / sulfonic group content resin which comes to carry out the copolymer of the phosphoric-acid radical content partial saturation monomer which has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular, and the sulfonic group content partial saturation monomer which has one or more sulfonic groups and one or more ethylene nature unsaturated bonds in intramolecular.
[Claim 2] the solid-state polyelectrolyte film according to claim 1 — setting — said phosphoric-acid radical content partial saturation monomer — following general formula (A): — [Formula 1]

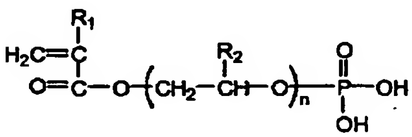

··· (A)

(— however, R1 is hydrogen or an alkyl group, R2 is an alkyl group which is not permuted [hydrogen, a permutation or], and n is the integer of 1-6.) — solid-state polyelectrolyte film characterized by what is expressed.
[Claim 3] It is the solid-state polyelectrolyte film which R1 is H or CH3, and is characterized by R2 being H, CH3, or CH2Cl in the solid-state polyelectrolyte film according to claim 2.
[Claim 4] Solid-state polyelectrolyte film characterized by said sulfonic group content partial saturation monomer being p-styrene sulfonic acid in the solid-state polyelectrolyte film according to claim 1 to 3.
[Claim 5] The approach characterized by copolymerizing after casting the mixture of the phosphoric-acid radical content partial saturation monomer which is the approach of manufacturing the solid-state polyelectrolyte film which has the proton conductivity it is nonconducting from a phosphoric-acid radical / sulfonic group content resin, and has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular, and the sulfonic group content partial saturation monomer which has one or more sulfonic groups and one or more ethylene nature unsaturated bonds in intramolecular.
[Claim 6] The approach which adds a photopolymerization initiator into the mixture of said phosphoric-acid radical content partial saturation monomer and said sulfonic group content partial saturation monomer, and is characterized by copolymerizing said phosphoric-acid radical content partial saturation monomer and said sulfonic group content partial saturation monomer by covering one [at least] field with a diactinism plate, and irradiating ultraviolet rays in an approach according to claim 5 after casting the obtained constituent on a shaping die.
[Claim 7] an approach according to claim 5 or 6 — setting — said phosphoric-acid radical content partial saturation monomer — following general formula (A): — [Formula 2]

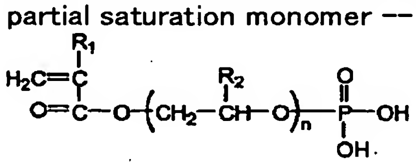

··· (A)

(— however, R1 is hydrogen or an alkyl group, R2 is an alkyl group which is not permuted [hydrogen, a permutation or], and n is the integer of 1-6.) — approach characterized by what is expressed.
[Claim 8] It is the approach which R1 is H or CH3, and is characterized by R2 being H, CH3, or CH2Cl in an approach according to claim 7.

[Claim 9] The approach characterized by said sulfonic group content partial saturation monomer being p-styrene sulfonic acid in an appr[redacted]h according to claim 5 to 8.
[Claim 10] Solid-state polyelec[redacted]te bipolar membrane which has the pr[redacted] conductivity characterized by consisting of phosphoric-acid radical content resin and a reinforcement sheet.
[Claim 11] Solid-state polyelectrolyte bipolar membrane characterized by being the proton conductivity solid-state macromolecule with which said phosphoric-acid radical content resin comes to carry out the polymerization of the phosphoric-acid radical content partial saturation monomer which has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular in solid-state polyelectrolyte bipolar membrane according to claim 10.
[Claim 12] solid-state polyelectrolyte bipolar membrane according to claim 10 or 11 -- setting -- said phosphoric-acid radical content partial saturation monomer -- following general formula (A): -- [Formula 3]

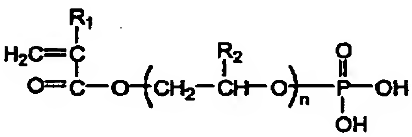

··· (A)

(-- however, R1 is hydrogen or an alkyl group, R2 is an alkyl group which is not permuted [hydrogen, a permutation or], and n is the integer of 1-6.) -- solid-state polyelectrolyte bipolar membrane characterized by what is expressed.
[Claim 13] It is the solid-state polyelectrolyte bipolar membrane which R1 is H or CH3, and is characterized by R2 being H, CH3, or CH2Cl in solid-state polyelectrolyte bipolar membrane according to claim 12.
[Claim 14] Solid-state polyelectrolyte bipolar membrane characterized by being the sheet with which said reinforcement sheet consists of fiber of minerals or the quality of organic in solid-state polyelectrolyte bipolar membrane according to claim 10 to 13.
[Claim 15] Solid-state polyelectrolyte bipolar membrane characterized by said reinforcement sheet being textile fabrics, a nonwoven fabric, or paper in solid-state polyelectrolyte bipolar membrane according to claim 14.
[Claim 16] Solid-state polyelectrolyte bipolar membrane characterized by said reinforcement sheet being a resin film in solid-state polyelectrolyte bipolar membrane according to claim 10 to 13.
[Claim 17] Solid-state polyelectrolyte bipolar membrane characterized by said resin film being fine porosity in solid-state polyelectrolyte bipolar membrane according to claim 16.
[Claim 18] The approach characterized by whether to infiltrate into a reinforcement sheet the phosphoric-acid radical content partial saturation monomer which is the approach of manufacturing the solid-state polyelectrolyte bipolar membrane which has the proton conductivity it is nonconducting from phosphoric-acid radical content resin and a reinforcement sheet, and has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular, and carrying out the polymerization of said phosphoric-acid radical content partial saturation monomer after applying.
[Claim 19] The approach characterized by carrying out the polymerization of said phosphoric-acid radical content partial saturation monomer whether the constituent containing said phosphoric-acid radical content partial saturation monomer and a photopolymerization initiator is infiltrated into a reinforcement sheet in an approach according to claim 18, and by inserting said reinforcement sheet into the support substrate of diactinism, and irradiating ultraviolet rays after applying.
[Claim 20] an approach according to claim 18 or 19 -- setting -- said phosphoric-acid radical content partial saturation monomer -- following general formula (A): -- [Formula 4]


··· (A)

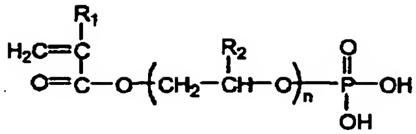
(-- however, R1 is hydrogen or an alkyl group, R2 is an alkyl group which is not permuted [hydrogen, a permutation or], and n is the integer of 1-6.) -- approach characterized by what is expressed.
[Claim 21] It is the approach which R1 is H or CH3, and is characterized by R2 being H, CH3, or CH2Cl in an approach according to claim 20.
[Claim 22] The approach characterized by being the sheet with which said reinforcement sheet consists of fiber of minerals or the quality of organic in an approach according to claim 18 to 21.
[Claim 23] The approach characterized by said reinforcement sheet being textile fabrics, a nonwoven

fabric, or paper in an approach according to claim 22.
[Claim 24] The approach characterized by said reinforcement sheet being a resin film in an approach according to claim 18 to 21.
[Claim 25] The approach characterized by said resin film being fine porosity in an approach according to claim 24.
[Claim 26] Solid-state polyelectrolyte bipolar membrane which has the proton conductivity characterized by consisting of a phosphoric-acid radical / sulfonic group content resin, and a reinforcement sheet..
[Claim 27] It is the solid-state polyelectrolyte bipolar membrane characterized by being the copolymer of the phosphoric-acid radical content partial saturation monomer to which said phosphoric-acid radical / sulfonic group content resin have one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular in solid-state polyelectrolyte bipolar membrane according to claim 26, and the sulfonic group content partial saturation monomer which has one or more sulfonic groups and one or more ethylene nature unsaturated bonds in intramolecular.
[Claim 28] solid-state polyelectrolyte bipolar membrane according to claim 26 or 27 -- setting -- said phosphoric-acid radical content partial saturation monomer -- following general formula (A): -- [Formula 5]



··· (A)

(-- however, R1 is hydrogen or an alkyl group, R2 is an alkyl group which is not permuted [hydrogen, a permutation or], and n is the integer of 1-6.) -- solid-state polyelectrolyte bipolar membrane characterized by what is expressed.
[Claim 29] It is the solid-state polyelectrolyte bipolar membrane which R1 is H or CH3, and is characterized by R2 being H, CH3, or CH2Cl in solid-state polyelectrolyte bipolar membrane according to claim 28.
[Claim 30] Solid-state polyelectrolyte bipolar membrane characterized by said sulfonic group content partial saturation monomer being p-styrene sulfonic acid in solid-state polyelectrolyte bipolar membrane according to claim 26 to 29.
[Claim 31] Solid-state polyelectrolyte bipolar membrane characterized by being the sheet with which said reinforcement sheet consists of fiber of minerals or the quality of organic in solid-state polyelectrolyte bipolar membrane according to claim 26 to 30.
[Claim 32] Solid-state polyelectrolyte bipolar membrane characterized by said reinforcement sheet being textile fabrics, a nonwoven fabric, or paper in solid-state polyelectrolyte bipolar membrane according to claim 31.
[Claim 33] Solid-state polyelectrolyte bipolar membrane characterized by said reinforcement sheet being a resin film in solid-state polyelectrolyte bipolar membrane according to claim 26 to 30.
[Claim 34] Solid-state polyelectrolyte bipolar membrane characterized by said resin film being fine porosity in solid-state polyelectrolyte bipolar membrane according to claim 33.
[Claim 35] It is the approach of manufacturing the solid-state polyelectrolyte bipolar membrane which has the proton conductivity it is nonconducting from a phosphoric-acid radical / sulfonic group content resin, and a reinforcement sheet. The phosphoric-acid radical content partial saturation monomer which has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular, The constituent containing the sulfonic group content partial saturation monomer which has one or more sulfonic groups and one or more ethylene nature unsaturated bonds in intramolecular The approach characterized by whether to infiltrate a reinforcement sheet and copolymerizing said phosphoric-acid radical content partial saturation monomer and said sulfonic group content partial saturation monomer after applying.
[Claim 36] The approach characterized by copolymerizing said phosphoric-acid radical content partial saturation monomer and said sulfonic group content partial saturation monomer whether the constituent containing said phosphoric-acid radical content partial saturation monomer, said sulfonic group content partial saturation monomer, and a photopolymerization initiator is infiltrated into a reinforcement sheet in an approach according to claim 35, and by inserting said reinforcement sheet into the support substrate of diactinism, and irradiating ultraviolet rays after applying.
[Claim 37] an approach according to claim 35 or 36 -- setting -- said phosphoric-acid radical content partial saturation monomer -- following general formula (A): -- [Formula 6]



A)

(— however, R1 is hydrogen or an alkyl group, R2 is an alkyl group which is not permuted [hydrogen, a permutation or], and n is the integer of 1−6.) — approach characterized by what is expressed.

[Claim 38] It is the approach which R1 is H or CH3, and is characterized by R2 being H, CH3, or CH2Cl in an approach according to claim 37.

[Claim 39] The approach characterized by said sulfonic group content partial saturation monomer being p-styrene sulfonic acid in an approach according to claim 35 to 38.

[Claim 40] The approach characterized by being the sheet with which said reinforcement sheet consists of fiber of minerals or the quality of organic in an approach according to claim 35 to 39.

[Claim 41] The approach characterized by said reinforcement sheet being textile fabrics, a nonwoven fabric, or paper in an approach according to claim 40.

[Claim 42] The approach characterized by said reinforcement sheet being a resin film in an approach according to claim 35 to 39.

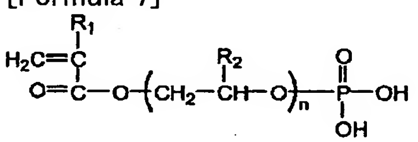
[Claim 43] The approach characterized by said resin film being fine porosity in an approach according to claim 42.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] Without using especially an organic solvent about the suitable solid-state polyelectrolyte (compound) film for electrolyte membranes, such as a primary cell, a rechargeable battery, and a fuel cell, a display device, various sensors, a signal transduction medium, a solid-state capacitor, ion exchange membrane, etc., and its manufacture approach, this invention is excellent in thermal resistance, chemical resistance, and dimensional stability, and relates to the solid-state polyelectrolyte (compound) film in which high proton conductivity is shown over a large temperature requirement and a large humidity requirement, and its manufacture approach.
[0002]
[Description of the Prior Art] The polymer which belongs to the so-called cation exchange resin as a solid-state polyelectrolyte ingredient, For example, polystyrene sulfonate, a polyvinyl sulfonic acid, a perfluoro sulfonic-acid polymer, Perfluoro carboxylic-acid polymer [Polymer Preprints, Japan Vol.42, No.7, and pp.2490-2492 (1993), Polymer Preprints, Japan Vol.43, No.3, and pp.735-736 (1994), Polymer Preprints and Japan Vol. -- 42, No.3, and pp.730 (1993)] etc. -- it is reported.
[0003] Since it combines with specific ion firmly or the solid-state polymeric materials which have a sulfonic group especially in a side chain have the property which penetrates a cation or an anion alternatively, they are fabricated the shape of a particle, fibrous, or in the shape of film, and are used for various kinds of applications, such as electrodialysis film, diffusion-dialysis film, and a cell diaphragm. The fluorine system polyelectrolyte film which has a sulfonic group especially in the side chain of a perfluoro frame known for the trademark of Nafion (product made from DuPont) is excellent in thermal resistance and chemical resistance, and is put in practical use as an electrolyte membrane which is equal to the use under severe conditions. However, since the above fluorine system electrolyte membranes are difficult to manufacture, it has the problem of being very expensive.
[0004] The solid-state polyelectrolyte which, on the other hand, introduced the alkyl sulfonic group or the alkyl phosphoric-acid radical into the heat resistant resin which has hydrocarbon frames, such as polybenzimidazole, is also reported (JP,9-87570,A, JP,9-110982,A). This solid-state polyelectrolyte has the outstanding thermal resistance (weight reduction initiation temperature: 250 degrees C or more) while showing high conductivity (10-4-10-2Scm-1) also under a 100-degree C elevated temperature in a moisture state, but when conductivity is not shown in the state of anhydrous, in case it creates a cast film, harmful solvents, such as dimethylacetamide, must be used for it. Moreover, since heat resistant resin, such as polybenzimidazole, is very expensive, there are many problems as general-purpose ingredients, such as the point of cost performance to an automotive fuel cell. Moreover, since not only a polybenzimidazole frame but the resin which generally has a hydrocarbon frame is inferior to anti-oxidation degradation nature, it is reported that a problem is in endurance (JP,2000-11755,A). A solid-state polyelectrolyte which has further more high conductivity is desired.
[0005]
[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is offering the solid-state polyelectrolyte film excellent in thermal resistance and chemical resistance, and its manufacture approach while having sufficient high conductivity to use it for a fuel cell etc.
[0006] Another purpose of this invention is offering the solid-state polyelectrolyte bipolar membrane excellent in endurance, such as a mechanical strength and thermal resistance, chemical resistance, and dimensional stability, and its manufacture approach while having sufficient high conductivity to use it for a fuel cell.

[0007]
[Means for Solving the Problem] [illegible]iew of the above-mentioned purpose, [illegible]eheartedly, as a result of research, the solid-state polyelectrolyte film which consists of a copolymer of the phosphoric-acid radical content partial saturation monomer to which this invention person etc. has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular, and the sulfonic group content partial saturation monomer which has one or more sulfonic groups and one or more ethylene nature unsaturated bonds in intramolecular had remarkably high conductivity, conductive temperature dependence was low, and it discovered excelling in thermal resistance and chemical resistance. It discovered that the solid-state polyelectrolyte bipolar membrane excellent in the mechanical strength and endurance which show high proton conductivity over a large temperature requirement and a large humidity requirement was obtained, without using an organic solvent whether this invention person etc. infiltrates the constituent containing a phosphoric-acid radical content partial saturation monomer (or a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer) and a polymerization initiator into a reinforcement sheet again, and by carrying out a polymerization, after applying. This invention is completed based on this invention.
[0008] That is, the solid-state polyelectrolyte film of this invention is characterized by consisting of a phosphoric-acid radical / sulfonic group content resin which comes to carry out the copolymer of the phosphoric-acid radical content partial saturation monomer which has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular, and the sulfonic group content partial saturation monomer which has one or more sulfonic groups and one or more ethylene nature unsaturated bonds in intramolecular.
[0009] as a phosphoric-acid radical content partial saturation monomer -- following general formula (A): -- [Formula 7]


... (A)

(-- however, R1 is hydrogen or an alkyl group, R2 is an alkyl group which is not permuted [hydrogen, a permutation or], and n is the integer of 1-6.) -- what is expressed is desirable. R1 is H or CH3, and, as for R2, it is desirable that they are H, CH3, or CH2Cl.
[0010] As for a sulfonic group content partial saturation monomer, it is desirable that it is p-styrene sulfonic acid.
[0011] After the method of manufacturing the solid-state polyelectrolyte film which has the proton conductivity it is nonconducting from a phosphoric-acid radical / sulfonic group content resin casts the mixture of the phosphoric-acid radical content partial saturation monomer which has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular, and the sulfonic group content partial saturation monomer which has one or more sulfonic groups and one or more ethylene nature unsaturated bonds in intramolecular, it is characterized by copolymerizing.
[0012] After adding a photopolymerization initiator into the mixture of a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer and casting the obtained constituent on a shaping die, it is desirable by covering one [at least] field with a diactinism plate, and irradiating ultraviolet rays to copolymerize a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer.
[0013] First solid-state polyelectrolyte bipolar membrane which has the proton conductivity of this invention is characterized by consisting of phosphoric-acid radical content resin and a reinforcement sheet. As for phosphoric-acid radical content resin, it is desirable that it is the proton conductivity solid-state macromolecule which comes to carry out the polymerization of the phosphoric-acid radical content partial saturation monomer which has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds to intramolecular. As for a reinforcement sheet, it is desirable that it is the sheet which consists of fiber of minerals or the quality of organic. Moreover, as for a reinforcement sheet, it is desirable that they are textile fabrics, a nonwoven fabric, paper, or a resin film. As for a resin film, it is desirable that it is fine porosity.
[0014] Whether the phosphoric-acid radical content partial saturation monomer which has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular is infiltrated into a reinforcement sheet, and after the approach of this invention of manufacturing the first solid-state polyelectrolyte bipolar membrane which has the proton conductivity it is nonconducting from phosphoric-

acid radical content resin and a reinforcement sheet applies, it is characterized by carrying out the polymerization of the phosphoric-acid radical content partial saturation monomer.

[0015] In the above-mentioned approach, whether the constituent containing a phosphoric-acid radical content partial saturation monomer and a photopolymerization initiator is infiltrated into a reinforcement sheet, and after applying, it is desirable by inserting a reinforcement sheet into the support substrate of diactinism, and irradiating ultraviolet rays to carry out the polymerization of the phosphoric-acid radical content partial saturation monomer.

[0016] Second solid-state polyelectrolyte bipolar membrane which has the proton conductivity of this invention is characterized by consisting of a phosphoric-acid radical / sulfonic group content resin, and a reinforcement sheet. As for a phosphoric-acid radical / sulfonic group content resin, it is desirable that it is the copolymer of the phosphoric-acid radical content partial saturation monomer which has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular, and the sulfonic group content partial saturation monomer which has one or more sulfonic groups and one or more ethylene nature unsaturated bonds in intramolecular.

[0017] The approach of manufacturing the second solid-state polyelectrolyte bipolar membrane which has the proton conductivity it is nonconducting from a phosphoric-acid radical / sulfonic group content resin, and a reinforcement sheet The phosphoric-acid radical content partial saturation monomer which has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular, The constituent containing the sulfonic group content partial saturation monomer which has one or more sulfonic groups and one or more ethylene nature unsaturated bonds in intramolecular Whether a reinforcement sheet is infiltrated and after applying, it is characterized by copolymerizing a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer.

[0018] In the above-mentioned approach, whether the constituent containing a phosphoric-acid radical content partial saturation monomer, a sulfonic group content partial saturation monomer, and a photopolymerization initiator is infiltrated into a reinforcement sheet, and after applying, it is desirable by inserting a reinforcement sheet into the support substrate of diactinism, and irradiating ultraviolet rays to copolymerize a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer.

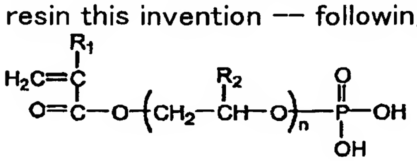
[0019] While the first [of this invention] and second solid-state polyelectrolyte bipolar membrane is all 30-80-degree C temperature requirements in a moisture state and shows the high conductivity of the range of 10-5-10-2 Scm-1, weight reduction initiation temperature has the outstanding thermal resistance of 200 degrees C or more, and does not cause change of appearances, such as telescopic motion, curvature, and interlaminar peeling, in the range of 30-100 degrees C, but shows the outstanding dimensional stability. The conductive temperature dependence of especially the solid-state polyelectrolyte bipolar membrane containing a phosphoric-acid radical / sulfonic group content resin is notably low, and the temperature requirement which is 30-80 degrees C shows the high conductivity of the range of 10-3-10-2 Scm-1.

[0020] Moreover, in preparing the proton conductivity polyelectrolyte film, the polyelectrolyte prepared beforehand is dissolved in an organic solvent, and by the manufacture approach of this invention, ultraviolet rays are irradiated at a monomer constituent, and with a conventional method, the place which carries out cast film production, since copolymerization is carried out, it is released from a polymerization or the complicatedness which deals with an organic solvent.

[0021]

[Embodiment of the Invention] Hereafter, the proton conductivity solid-state polyelectrolyte (compound) film containing the phosphoric-acid radical content resin of this invention, or a phosphoric-acid radical / sulfonic group content resin and those manufacture approaches are explained to a detail.

[I] the phosphoric-acid radical content resin, and the phosphoric-acid radical / sulfonic group content resin used for phosphoric-acid radical content resin, and a phosphoric-acid radical / sulfonic group content resin this invention -- following general formula (A): -- [Formula 8]



··· (A)

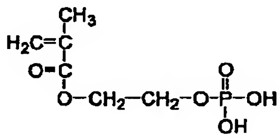
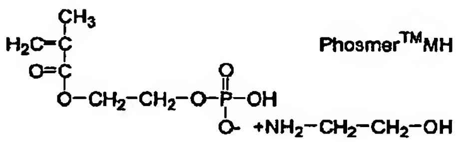
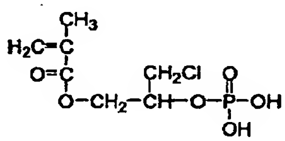
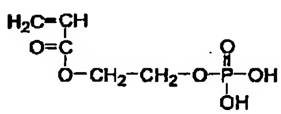
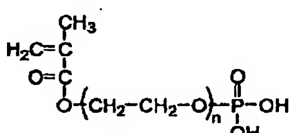
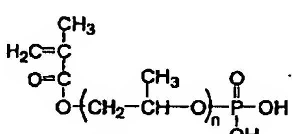
(-- however, R1 is hydrogen or an alkyl group, R2 is an alkyl group which is not permuted [hydrogen, a permutation or], and n is the integer of 1-6.) -- the phosphoric-acid radical content partial saturation monomer expressed -- an indispensable component -- carrying out -- a polymerization -- or it

copolymerizes. R1 is H or CH3, and as for R2, it is desirable that they are H, CH3, or CH2Cl. The above-mentioned phosphoric-acid radical content partial saturation monomer may be copolymerized with this and other partial saturation monomers which may be copolymerized.

[0022] (1) The structure expression of the monomer which can be used suitable for this invention among the phosphoric-acid radical content partial saturation monomers expressed by the phosphoric-acid radical content partial saturation monomer general formula (A) is shown in Table 1, and the physical properties of these monomers are shown in Table 2. these monomers -- uni-chemical one -- Co., Ltd. -- from -- it is sold as a trade name PhosmerTM. However, the phosphoric-acid radical content partial saturation monomer which can be used for this invention is not limited to these.

[0023]

[Table 1]

名称	構造式	グレード名
アシッド・ホスホオキシエチルメタクリレート		Phosmer™M
メタクロイル・オキシエチルアシッドホスフェート・モノエタノールアミン塩		Phosmer™MH
3-クロロ-2-アシッド・ホスホオキシプロピルメタクリレート		Phosmer™CL
アシッド・ホスホオキシエチルアクリレート		Phosmer™A
アシッド・ホスホオキシポリオキシエチレングリコールモノメタクリレート	 n=4~5	Phosmer™PE
アシッド・ホスホオキシポリオキシプロピレングリコールメタクリレート	 n=5~6	Phosmer™PP

[0024]

[Table 2]

グレード (Phosmer™)		M	MH	CL	A	PE	PP
分子量(g)/ﾘﾝ酸当量(g)		210	271	258.5	196	333	440
比重 (at 20℃)		1.392	1.302	1.453	1.468	1.248	1.157
屈折率 (nd at 20 °C)		1.4562	1.4815	1.4785	1.4664	1.4696	1.4577
粘度 (poise at 20 °C) Brookfield型粘度計 (ﾛｰﾀ No.) により測定		80 (No. 1)	800 (No. 2)	700 (No. 2)	320 (No. 2)	25 (No. 1)	55 (No. 2)
酸化	理論値	533.3	206.6	433.3	571.4	—	—
	実測値	500以下	196	410以下	—	320	255
製品のpH		—	9.4	—	—	—	—
水溶性	(wt % at 20℃)	4.1	4.3	1.3	9.4	—	—
	(wt % at 25℃)	—	—	—	—	4.0	3.2
単量体が可溶な溶媒		有機酸, ｹﾄﾝ, ｱﾙｺｰﾙ	2-ﾋﾄﾞﾛｷｼｴﾁﾙ ﾒﾀｸﾘﾚｰﾄ, ﾒﾀﾉｰﾙ, ｴﾀﾉｰﾙ, ｲｿﾌﾟﾛﾋﾟﾙｱﾙｺｰﾙ, ｱｸﾘﾙ酸, 酢酸	有機酸, ｹﾄﾝ, ｱﾙｺｰﾙ	同左	同左	ﾍﾞﾝｾﾞﾝ, ﾄﾙｴﾝ, ｷｼﾚﾝ

[0025] The phosphoric-acid radical content partial saturation monomer of a general formula (A) may be used independently, and may use two or more sorts together.
[0026] (2) Other partial saturation monomer above-mentioned phosphoric-acid radical content partial saturation monomers which may be copolymerized, and the partial saturation monomer which may be copolymerized can be divided roughly into the following two groups (2-1) and (2-2).
[0027] (2-1) The partial saturation monomer containing the partial saturation monomer acid radical containing an acid radical is a compound which has at least one acid radical and at least one ethylene nature unsaturated bond in intramolecular. A sulfonic group, a carboxylic-acid radical, etc. are mentioned as an acid radical. Among these, a sulfonic group content partial saturation monomer is desirable, and a phosphoric-acid radical / sulfonic group content resin is obtained by copolymerization of a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer. Its conductive temperature dependence is notably low while the solid-state polyelectrolyte (compound) film containing a phosphoric-acid radical / sulfonic group content resin has the further excellent conductivity.
[0028] As an example of a sulfonic group content partial saturation monomer, an allyl compound sulfonic acid, a meta-allyl compound sulfonic acid, a vinyl sulfonic acid, p-styrene sulfonic acid, a butyl acrylate (meta)-4-sulfonic acid, an AKURIRO (meta) oxybenzene sulfonic acid, t-butyl acrylamide sulfonic acid, 2-acrylic-2-acrylamido-2-methyl propane sulfonic acid, etc. are mentioned. p-styrene sulfonic acid is desirable especially. However, since the allyl group starts degradative chaintransfer, as for an allyl compound sulfonic acid and a meta-allyl compound sulfonic acid, it is desirable to make the amount used into less than 65 % of the weight. These sulfonic group content partial saturation monomers may be independent, and may use two or more sorts together. As an example of a carboxylic-acid radical content partial saturation monomer, an acrylic acid (meta), a crotonic acid, a maleic acid, a fumaric acid, an itaconic acid, a maleic-acid anhydride, etc. are mentioned. These carboxylic-acid radical content partial saturation monomers may be independent, and may use two or more sorts together.
[0029] (2-2) Partial saturation monomer which does not contain an acid radical (2-1) Although it is except having indicated and not a gas but all the partial saturation monomers that have one or more ethylene nature unsaturated bonds in intramolecular are contained in this partial saturation monomer in ordinary temperature, acrylonitrile, acrylic ester (meta), and the styrene that is not permuted [a permutation or] are suitable especially (meta). It is desirable to use ethylene GURIKORUJI (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, hexamethylene JIORUJI (meta) acrylate, a divinylbenzene, etc. which contain two or more ethylene nature unsaturated bonds in 1 intramolecular in order to improve the chemical resistance of the solid-state polyelectrolyte (compound) film.
[0030] (3) Weight ratio phosphoric-acid radical content partial saturation monomer of each partial saturation monomer (1) Other partial saturation monomers (2) Weight ratio (1) / (2) Although it is the range

of 100 / 0 - 20/80, it is (1)/(2) preferably. = it is 80 / 20 - 50/50. Moreover, other partial saturation monomers (2) Partial saturation monomer which contains an acid radical include (2-1) The other partial saturation monomer (2-2) A weight ratio brings the plus effectiveness to proton conductivity (2-1). It is desirable to consider as the range of (2-1) / (2-2) = 100 / 0 - 50/50 so that it may become dominant. therefore, the case where a sulfonic group content partial saturation monomer is used as a partial saturation monomer (2-1) containing especially an acid radical -- the weight ratio of a phosphoric-acid radical content partial saturation monomer / sulfonic group content partial saturation monomer -- 100 / 0 - 20/80 -- it is 80 / 20 - 50/50 preferably, and the weight ratios of an acid radical content partial saturation monomer besides sulfonic group content partial saturation monomer/are 100 / 0 - 50/50.
[0031] [II] As a photopolymerization initiator added to a monomer constituent by photopolymerization initiator this invention (1) -- R-(CO) x-R' (R, R' = hydrogen, or a hydrocarbon group --) the contiguity poly ketone compounds (for example, diacetyl --) expressed by x = 2-3 (2), such as dibenzyl a-carbonyl alcohols expressed by R-CO-CHOH-R' (R and R' = hydrogen or hydrocarbon group) (for example, benzoin etc.), (3) Acyloin ether expressed by R-CH(OR")-CO-R' (R, R', R"= hydrocarbon group) (for example, benzoin methyl ether etc.), (4) a-permutation acyloins (for example, a-alkyl benzoin etc.) expressed by Ar-CR(OH)-CO-Ar (Ar = aryl group and R = hydrocarbon group) and (5) There are polykaryotic quinones (for example, 9, 10-Anthraquinone, etc.). These photopolymerization initiators are independent respectively, or can be used together and used.
[0032] the amount of the photopolymerization initiator used -- the sum total weight of a partial saturation monomer -- receiving -- 0.5 - 5% of the weight of the range -- it is 1 - 3% of the weight of the range preferably. If it is less than 0.5 % of the weight, since a polymerization or copolymerization will not be completed in predetermined UV irradiation time amount but an unreacted monomer will remain, it is not desirable. Moreover, the polymerization degree of the resin obtained with super-** 5% of the weight is too low, and since the amount of the photopolymerization initiator used is in the inclination which resin colors, it is not desirable.
[0033] By this invention, the dissolution into the monomer mixture of a photopolymerization initiator is made easy, the viscosity of a partial saturation monomer is lowered and it makes it easy to sink in to a reinforcement sheet, and the coating weight to a reinforcement sheet is made to decrease, and low boilers, such as a methanol and an acetone, may be added as a diluent for the purpose, such as making thin thickness of the solid-state polyelectrolyte (compound) film.
[0034] [III] The reinforcement sheet used for reinforcement sheet this invention can be divided roughly into the three following groups.
(1) The textile fabrics which consist of the sheet glass fiber which consists of an inorganic fiber, an alumina fiber, rock wool fiber, slag fiber, etc., a nonwoven fabric, paper, etc. are mentioned. the basis weight of the sheet which consists of an inorganic fiber -- 10 - 60 mg/cm2 -- desirable -- 10 - 40 mg/cm2 -- it is -- thickness -- 1-60 mum -- desirable -- 5-40 It is the range of mum.
[0035] (2) The textile fabrics which consist of the sheet nylon fiber which consists of organic fiber, polyester fiber, an acrylic fiber, an aramid fiber, etc., a nonwoven fabric, paper, etc. are mentioned. However, since the temperature of the solid-state polyelectrolyte (compound) film may rise to about 100 degrees C at the time of UV irradiation, it is required to have sufficient thermal resistance to bear it. The basis weight and thickness of a sheet it is thin from organic fiber are the same as the case of (1). However, when the monomer constituent sunk in or applied contains the partial saturation monomer which has strong acid radicals, such as a sulfonic group, since the textile fabrics which consist of nylon fiber, a nonwoven fabric, paper, etc. have weak acid resistance, they are unsuitable.
[0036] (3) As a resin film which sinks in or applies a resin film monomer constituent, films, such as polyethylene resin, polypropylene resin, Pori 3-methyl pentene resin, nylon 6 resin, polyester resin, thermoplastic polyurethane, polysulfone resin, polyether sulphone resin, polyether ether ketone resin, aramid resin, polyimide resin, and fluorine system resin, are desirable. Although a fine porosity film or a nonporous film is sufficient as a resin film, the viewpoint of the impregnating ability of a monomer constituent to the former is desirable. However, when the monomer constituent to infiltrate contains the partial saturation monomer which has strong acid radicals, such as a sulfonic group, since acid resistance of a nylon film is not strong, it is unsuitable.
[0037] In the case of a fine porosity film, the smallest possible one of the aperture of a fine hole is desirable, and it is desirable that it is especially a diameter of submicron one. Moreover, the larger possible one of the hole density of the whole fine porosity film is desirable, and it is especially desirable that it is 40 - 50% (opposite surface area). The thickness of a resin film is 1-40. mum is desirable and it is 5-25. The range of mum is more desirable.

[0038] Although it changes greatly with absorptivity of a monomer constituent, if it puts in another way, as for the weight ratio of a reinforcement sheet / monomer constituent, generally it is [the weight ratio of a reinforcement sheet and a monomer constituent] desirable the compatibility over the monomer constituent of a reinforcement sheet and that it is the range of 1 / 20 - 1/2.
[0039] [IV] After casting the constituent containing both the partial saturation monomer and a photopolymerization initiator for a shaping die in the case of the solid-state polyelectrolyte film which consists of a manufacture approach phosphoric-acid radical content partial saturation monomer of the solid-state polyelectrolyte (compound) film, and a sulfonic group content partial saturation monomer and covering with a diactinism plate, it can manufacture by irradiating ultraviolet rays and carrying out copolymerization of both the partial saturation monomer.
[0040] Moreover, whether in the case of the solid-state polyelectrolyte bipolar membrane which consists of a phosphoric-acid radical content partial saturation monomer (or a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer) and a reinforcement sheet, the constituent containing a partial saturation monomer and a photopolymerization initiator is infiltrated into a reinforcement sheet, and after applying, it can manufacture by inserting a reinforcement sheet into the support substrate of diactinism, irradiating ultraviolet rays, and photopolymerizing a partial saturation monomer.
[0041] It does not paste up with the solid-state polyelectrolyte obtained by carrying out the polymerization of having the thermal resistance which bears the temperature up at the time of the polymerization by ultraviolet-rays permeability being not only high but UV irradiation, a partial saturation monomer constituent, and this, but two support substrates which sandwich this in carrying out the UV irradiation polymerization of the reinforcement sheet which sank in the partial saturation monomer constituent need for detachability to be good.
[0042] Usually, although the glass plate to be used is very good about ultraviolet-rays permeability and thermal resistance, since it sticks with the solid-state polyelectrolyte obtained by the polymerization or copolymerization of a partial saturation monomer used for this invention, it is desirable to use it, after applying the remover of a silicone system or a fluorine system to the front face of a glass plate beforehand or sticking the thin bright film of a fluororesin system.
[0043] The resin plate which has the thermal resistance of 100 degrees C or more with sufficient ultraviolet-rays permeability, such as Pori 3-methyl pentene [besides fluorine system resin, such as polyperfluoro vinyl ether resin (PFA) and polyvinylidene fluoride resin (PVDF),] resin and polypropylene resin, in addition to a glass plate can be used.
[0044] In performing UV irradiation on both sides of whether it covers with a diactinism plate and UV irradiation is performed or a partial saturation monomer constituent is infiltrated, and the applied reinforcement sheet between two support substrates, after casting a partial saturation monomer constituent, it is necessary to press out air and an excessive partial saturation monomer constituent out of a system. For example, when using a reinforcement sheet, it is desirable to perform UV irradiation, keeping it level in the condition of having stopped by the clip or the clamp, having put the pressure equally between two support substrates, as shown in drawing 1 . the UV irradiation reinforcement at the time of photopolymerization -- 5 - 50 mW/cm2 -- it considers as 10 - 25 mW/cm2 preferably.
[0045] the thickness of the solid-state polyelectrolyte (compound) film -- 300 below mum -- desirable -- 10-100 mum -- more -- desirable -- 10-30 It is referred to as mum.
[0046]
[Example] Although the following examples explain this invention to a detail further, this invention is not limited to these.
[0047] After adding the methanol to the partial saturation monomer constituent shown in one to examples 1-16 and example of comparison 4 table 3 as a diluent and adjusting viscosity to it, 2% of the weight of the IRUGA cure 651 (2 and 2-dimethoxy -1, 2-bibenzyl-1-ON) and 1% of the weight of the IRUGA cure 500 (1-hydroxy cyclohexyl phenyl ketone + benzophenone) were dissolved as a photopolymerization initiator, having used the whole partial saturation monomer as 100 % of the weight. After adopting various kinds of nonwoven fabrics or papers as a reinforcement sheet and infiltrating a partial saturation monomer constituent into a reinforcement sheet, as shown in drawing 1 and drawing 2 , it is partial saturation monomer constituent sinking-in reinforcement sheet **** between two glass plates which applied the silicone remover. Using the high pressure mercury vapor lamp (the toss cure 400 by Toshiba Electric Equipment Corp., and HC-0411 mold), the predetermined time exposure of the ultraviolet rays of 20 mW/cm2 was carried out, photopolymerization of the partial saturation monomer constituent was carried out to the partial saturation monomer constituent sinking-in reinforcement sheet, and solid-state

polyelectrolyte bipolar membrane was produced. The class of a partial satur[illegible]ion monomer constituent and reinforcement sheet and a basis [illegible]ht, UV irradiation time amount, and th[illegible]scription of bipolar membrane are shown in Table 3.

[0048]

[Table 3]

例 No.		実施例 1			実施例 2			実施例 3	
不飽和単量体組成物 (wt. %)	Phosmer M	50			—			50	
	Phosmer PP	50			95			50	
	PSSA(1)	—			—			—	
	HDDA(2)	—			5			—	
希釈剤 MeOH (wt. %)		0	50	75	0	50	75	50	75
補強材シート	種類	GF 不織布 GHN-30CGL(3)			GF 不織布 GHN-30CGL			GF 不織布 GMC-050E(4)	
	坪量(mg/cm²)	30			30			50	
照射時間 [表＋裏 (sec)]		40 + 40			40 + 40			40 + 40	
複合膜	樹脂／補強材シート(10)	9.6	7.5	4.7	8.5	6.1	4.2	7.2	4.0
	平滑性	良好			良好			良好	
	ピンホール	ナシ			ナシ			ナシ	
	厚さ(μm)	170	140	110	160	130	110	170	120
	導電率測定の有無	No			No			Yes	No

[0049] Table 3 continuation

例 No.		実施例 4		実施例 5	実施例 6
不飽和単量体組成物 (wt. %)	Phosmer M	—		50	—
	Phosmer PP	95		50	95
	PSSA(1)	—		—	—
	HDDA(2)	5		—	5
希釈剤 MeOH (wt. %)		50	75	75	50
補強材シート	種類	GF 不織布 GMC-050E		GF 紙(5)	GF 紙
	坪量(mg/cm²)	50		40	40
照射時間 [表＋裏 (sec)]		40 + 40		40 + 40	40 + 40
複合膜	樹脂／補強材シート(10)	6.0	5.0	4.5	5.3
	平滑性	良好		良好	良好
	ピンホール	ナシ		ナシ	ナシ
	厚さ(μm)	160	100	90	87
	導電率測定の有無	Yes	No	No	No

例 No.		実施例 7	実施例 8	実施例 9
不飽和単量体組成物 (wt. %)	Phosmer M	50	—	50
	Phosmer PP	50	95	50
	PSSA[1]	—	—	—
	HDDA[2]	—	5	—
希釈剤 MeOH (wt. %)		75	50	75
補強材シート	種類	PAN 紙[6]	PAN 紙	アラミド不織布 XL-1040[7]
	坪量(mg/cm²)	38	38	40
照射時間 [表＋裏 (sec)]		40 + 40	40 + 40	120 + 120
複合膜	樹脂／補強材シート[10]	3.8	5.0	13.3
	平滑性	良好	良好	良好
	ピンホール	ナシ	ナシ	ナシ
	厚さ(μm)	75	70	200
	導電率測定の有無	Yes	Yes	Yes

[0050] Table 3 continuation

例 No.		実施例 10	実施例 11	実施例 12
不飽和単量体組成物 (wt. %)	Phosmer M	—	50	—
	Phosmer PP	95	50	95
	PSSA[1]	—	—	—
	HDDA[2]	5	—	5
希釈剤 MeOH (wt. %)		50	75	50
補強材シート	種類	アラミド不織布 XL-1040	アラミド紙[8]	アラミド紙
	坪量(mg/cm²)	40	35	35
照射時間 [表＋裏 (sec)]		120 + 120	120 + 120	120 + 120
複合膜	樹脂／補強材シート[10]	10.1	5.6	4.7
	平滑性	良好	良好	良好
	ピンホール	ナシ	ナシ	ナシ
	厚さ(μm)	190	45	38
	導電率測定の有無	Yes	Yes	Yes

[0051] Table 3 continuation

例 No.		実施例 13	実施例 14	実施例 15
不飽和単量体組成物 (wt. %)	Phosmer M	50	—	50
	Phosmer PP	50	95	—
	PSSA(1)	—	—	50
	HDDA(2)	—	5	—
希釈剤 MeOH (wt. %)		50	50	70
補強材シート	種類	ハイポア 6022(9)	ハイポア 6022	GF 不織布 GHN-30CGL
	坪量(mg/cm²)	25	25	30
照射時間 [表+裏 (sec)]		40 + 40	40 + 40	60 + 60
複合膜	樹脂／補強材シート(10)	3.1	2.7	2.3
	平滑性	良好	良好	良好
	ピンホール	ナシ	ナシ	ナシ
	厚さ(μm)	37	20	104
	導電率測定の有無	No	No	Yes

[0052] Table 3 continuation

例 No.		実施例 16	比較例 1	比較例 2
不飽和単量体組成物 (wt. %)	Phosmer M	50	50	—
	Phosmer PP	—	50	95
	PSSA(1)	50	—	—
	HDDA(2)	—	—	5
希釈剤 MeOH (wt. %)		70	50	50
補強材シート	種類	ナイロンネット	—	—
	坪量(mg/cm²)	50	—	—
照射時間 [表+裏 (sec)]		60 + 60	40 + 40	40 + 40
複合膜	樹脂／補強材シート(10)	0.8	—	—
	平滑性	良好	良好	良好
	ピンホール	ナシ	ナシ	ナシ
	厚さ(μm)	約 100	約 30	約 20
	導電率測定の有無	Yes	No	No

[0053] Table 3 continuation

[0054] Table 3 continuation

例 No.		比較例 3	比較例 4
不飽和単量体組成物 (wt. %)	Phosmer M	—	—
	Phosmer PP	—	—
	PSSA(1)	100	100
	HDDA(2)	—	—
希釈剤 MeOH (wt. %)		82	82
補強材シート	種類	GF 不織布 GHN-30CGL	ナイロンネット
	坪量(mg/cm²)	30	50
照射時間 [表＋裏 (sec)]		60 + 60	60 + 60
複合膜	樹脂／補強材シート(10)	1.4	0.3
	平滑性	良好	良好
	ピンホール	ナシ	ナシ
	厚さ(μm)	52	100
	導電率測定の有無	Yes	Yes

Note : (1) PSSA: p-styrene sulfonic acid (2) HDDA: Hexamethylene diol diacrylate (3) GF (glass fiber) nonwoven fabric GHN-30CGL (commercial item by Oji Paper Co., Ltd.)
(4) GF (glass fiber) nonwoven fabric GMC-050E (commercial item by Oji Paper Co., Ltd.)
(5) GF (glass fiber) paper (prototype by Awa Paper Manufacturing Co., Ltd.)
(6) PAN (polyacrylonitrile) paper (prototype by Awa Paper Manufacturing Co., Ltd.)
(7) Aramid nonwoven fabric XL-1040 (prototype by Japan Vilene Co., Ltd.)
(8) Aramid paper (prototype by Awa Paper Manufacturing Co., Ltd.)
(9) PE (polyethylene) fine porosity film High pore TM 6022 (Asahi Chemical Industry Co., Ltd. make)
(10) The weight ratio of resin / reinforcing materials sheet.

[0055] About the typical solid-state polyelectrolyte bipolar membrane of an example and the example of a comparison, conductivity was measured at 90% of relative humidity, and 30-80 degrees C of temperature requirements. A result is shown in drawing 3 - drawing 5 .

[0056] If the approach of this invention is followed, even if it will use which reinforcement sheet from the result shown in drawing 3 - drawing 5 , a front face is smooth, and it turns out that solid-state polyelectrolyte bipolar membrane without a pinhole can be made. In addition, by using a diluent, the amount of resin adhering to a reinforcement sheet was able to be made into less than [1/several]. The thickness of the solid-state polyelectrolyte bipolar membrane of an example is 20-200. Although it is the range of mum, it can consider as desired thickness the basis weight of a reinforcement sheet, the compatibility of a reinforcement sheet and a partial saturation monomer constituent, the adhesion rate of resin, and by adjusting suitably the coating weight of a monomer constituent, and the pressure which presses it out, if it puts in another way.

[0057] It turns out that it is in a level good as a polyelectrolyte which the conductivity of the solid-state polyelectrolyte bipolar membrane of this invention is the order of 10-5-10-2 Scm-1, and makes a phosphoric-acid radical a functional group from the result shown in drawing 3 - drawing 5 . The conductive temperature dependence of especially the solid-state polyelectrolyte bipolar membrane (examples 15 and 16) containing the phosphoric-acid radical / sulfonic group content resin which consists of a copolymer of a phosphoric-acid radical content partial saturation monomer and p-styrene sulfonic acid was remarkably low, and the temperature requirement which is 30-80 degrees C showed 10-3-10-2 Scm-1 and high conductivity. On the other hand, since the solid-state polyelectrolyte bipolar membrane of the examples 3 and 4 of a comparison uses the homopolymer of p-styrene sulfonic acid, compared with the solid-state polyelectrolyte bipolar membrane of examples 15 and 16, its conductivity is low, and its conductive temperature dependence is high.

[0058] Although the above example showed the experimental result of the solid-state polyelectrolyte bipolar membrane which has a reinforcement sheet, it is clear to have the electrolyte property same as the solid-state polyelectrolyte film which does not have a reinforcement sheet. Therefore, the solid-state polyelectrolyte film which does not have a reinforcement sheet can be suitably used for the application as which a high mechanical strength is not required.
[0059]
[Effect of the Invention] [whether after casting the constituent containing a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer as explained in full detail above, copolymerization is carried out by UV irradiation etc., and] After sinking in or applying the constituent containing a phosphoric-acid radical content partial saturation monomer (or a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer) to a reinforcement sheet, by UV irradiation etc. a polymerization or by copolymerizing The solid-state polyelectrolyte (compound) film in which high proton conductivity is shown over a large temperature requirement and a large humidity requirement can be obtained without discharging an organic solvent. In the case of the solid-state polyelectrolyte bipolar membrane especially using a reinforcement sheet, it has the advantage of excelling in thermal resistance, chemical resistance, and dimensional stability.
[0060] Moreover, the solid-state polyelectrolyte (compound) film containing the phosphoric-acid radical / sulfonic group content resin which consists of a copolymer of a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer has still higher conductivity, and its conductive temperature dependence is low. The solid-state polyelectrolyte (compound) film of this invention which has such a description is suitable for solid-electrolyte membranes, such as a primary cell, a rechargeable battery, and a fuel cell, a display device, various sensors, a signal transduction medium, a solid-state capacitor, ion exchange membrane, etc.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] Without using especially an organic solvent about the suitable solid-state polyelectrolyte (compound) film for electrolyte membranes, such as a primary cell, a rechargeable battery, and a fuel cell, a display device, various sensors, a signal transduction medium, a solid-state capacitor, ion exchange membrane, etc., and its manufacture approach, this invention is excellent in thermal resistance, chemical resistance, and dimensional stability, and relates to the solid-state polyelectrolyte (compound) film in which high proton conductivity is shown over a large temperature requirement and a large humidity requirement, and its manufacture approach.

[Translation done.]

PRIOR ART

[Description of the Prior Art] The polymer which belongs to the so-called cation exchange resin as a solid-state polyelectrolyte ingredient For example, polystyrene sulfonate, a polyvinyl sulfonic acid, a perfluoro sulfonic-acid polymer, Perfluoro carboxylic-acid polymer [Polymer Preprints, Japan Vol.42, No.7, and pp.2490-2492 (1993), Polymer Preprints, Japan Vol.43, No.3, and pp.735-736 (1994), Polymer Preprints and Japan Vol. -- 42, No.3, and pp.730 (1993)] etc. -- it is reported.
[0003] Since it combines with specific ion firmly or the solid-state polymeric materials which have a sulfonic group especially in a side chain have the property which penetrates a cation or an anion alternatively, they are fabricated the shape of a particle, fibrous, or in the shape of film, and are used for various kinds of applications, such as electrodialysis film, diffusion-dialysis film, and a cell diaphragm. The fluorine system polyelectrolyte film which has a sulfonic group especially in the side chain of a perfluoro frame known for the trademark of Nafion (product made from DuPont) is excellent in thermal resistance and chemical resistance, and is put in practical use as an electrolyte membrane which is equal to the use under severe conditions. However, since the above fluorine system electrolyte membranes are difficult to manufacture, it has the problem of being very expensive.
[0004] The solid-state polyelectrolyte which, on the other hand, introduced the alkyl sulfonic group or the alkyl phosphoric-acid radical into the heat resistant resin which has hydrocarbon frames, such as polybenzimidazole, is also reported (JP,9-87570,A, JP,9-110982,A). This solid-state polyelectrolyte has the outstanding thermal resistance (weight reduction initiation temperature: 250 degrees C or more) while showing high conductivity (10-4-10-2Scm-1) also under a 100-degree C elevated temperature in a moisture state, but when conductivity is not shown in the state of anhydrous, in case it creates a cast film, harmful solvents, such as dimethylacetamide, must be used for it. Moreover, since heat resistant resin, such as polybenzimidazole, is very expensive, there are many problems as general-purpose ingredients, such as the point of cost performance to an automotive fuel cell. Moreover, since not only a polybenzimidazole frame but the resin which generally has a hydrocarbon frame is inferior to anti-oxidation degradation nature, it is reported that a problem is in endurance (JP,2000-11755,A). A solid-state polyelectrolyte which has further more high conductivity is desired.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] It is UV irradiation etc., after casting the constituent containing a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer as explained in full detail above. The solid-state polyelectrolyte (compound) film in which high proton conductivity is shown over a large temperature requirement and a large humidity requirement can be obtained without discharging an organic solvent a polymerization or by copolymerizing by UV irradiation etc., after sinking in or applying to a reinforcement sheet the constituent which is made to carry out copolymerization or contains a phosphoric-acid radical content partial saturation monomer (or a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer). In the case of the solid-state polyelectrolyte bipolar membrane especially using a reinforcement sheet, it has the advantage of excelling in thermal resistance, chemical resistance, and dimensional stability.
[0060] Moreover, the solid-state polyelectrolyte (compound) film containing the phosphoric-acid radical / sulfonic group content resin which consists of a copolymer of a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer has still higher conductivity, and its conductive temperature dependence is low. The solid-state polyelectrolyte (compound) film of this invention which has such a description is suitable for solid-electrolyte membranes, such as a primary cell, a rechargeable battery, and a fuel cell, a display device, various sensors, a signal transduction medium, a solid-state capacitor, ion exchange membrane, etc.

[Translation done.]

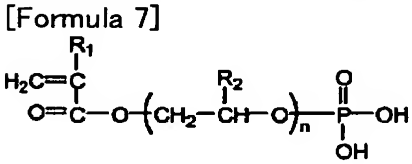
TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is offering the solid-state polyelectrolyte film excellent in thermal resistance and chemical resistance, and its manufacture approach while having sufficient high conductivity to use it for a fuel cell etc.
[0006] Another purpose of this invention is offering the solid-state polyelectrolyte bipolar membrane excellent in endurance, such as a mechanical strength and thermal resistance, chemical resistance, and dimensional stability, and its manufacture approach while having sufficient high conductivity to use it for a fuel cell.

[Translation done.]

MEANS

[Means for Solving the Problem] In view of the above-mentioned purpose, wholeheartedly, as a result of research, the solid-state polyelectrolyte film which consists of a copolymer of the phosphoric-acid radical content partial saturation monomer to which this invention person etc. has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular, and the sulfonic group content partial saturation monomer which has one or more sulfonic groups and one or more ethylene nature unsaturated bonds in intramolecular had remarkably high conductivity, conductive temperature dependence was low, and it discovered excelling in thermal resistance and chemical resistance. It discovered that the solid-state polyelectrolyte bipolar membrane excellent in the mechanical strength and endurance which show high proton conductivity over a large temperature requirement and a large humidity requirement was obtained, without using an organic solvent whether this invention person etc. infiltrates the constituent containing a phosphoric-acid radical content partial saturation monomer (or a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer) and a polymerization initiator into a reinforcement sheet again, and by carrying out a polymerization, after applying. This invention is completed based on this invention.
[0008] That is, the solid-state polyelectrolyte film of this invention is characterized by consisting of a phosphoric-acid radical / sulfonic group content resin which comes to carry out the copolymer of the phosphoric-acid radical content partial saturation monomer which has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular, and the sulfonic group content partial saturation monomer which has one or more sulfonic groups and one or more ethylene nature unsaturated bonds in intramolecular.
[0009] as a phosphoric-acid radical content partial saturation monomer -- following general formula (A): --
[Formula 7]



··· (A)

(-- however, R1 is hydrogen or an alkyl group, R2 is an alkyl group which is not permuted [hydrogen, a permutation or], and n is the integer of 1-6.) -- what is expressed is desirable. R1 is H or CH3, and, as for R2, it is desirable that they are H, CH3, or CH2Cl.
[0010] As for a sulfonic group content partial saturation monomer, it is desirable that it is p-styrene sulfonic acid.
[0011] After the method of manufacturing the solid-state polyelectrolyte film which has the proton conductivity it is nonconducting from a phosphoric-acid radical / sulfonic group content resin casts the mixture of the phosphoric-acid radical content partial saturation monomer which has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular, and the sulfonic group content partial saturation monomer which has one or more sulfonic groups and one or more ethylene nature unsaturated bonds in intramolecular, it is characterized by copolymerizing.
[0012] After adding a photopolymerization initiator into the mixture of a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer and casting the obtained constituent on a shaping die, it is desirable by covering one [at least] field with a diactinism plate, and irradiating ultraviolet rays to copolymerize a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer.
[0013] First solid-state polyelectrolyte bipolar membrane which has the proton conductivity of this invention is characterized by consisting of phosphoric-acid radical content resin and a reinforcement

sheet. As for phosphoric-acid radical content resin, it is desirable that it is the proton conductivity solid-state macromolecule which comes to carry out the polymerization of the phosphoric-acid radical content partial saturation monomer which has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds to intramolecular. As for a reinforcement sheet, it is desirable that it is the sheet which consists of fiber of minerals or the quality of organic. Moreover, as for a reinforcement sheet, it is desirable that they are textile fabrics, a nonwoven fabric, paper, or a resin film. As for a resin film, it is desirable that it is fine porosity.

[0014] Whether the phosphoric-acid radical content partial saturation monomer which has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular is infiltrated into a reinforcement sheet, and after the approach of this invention of manufacturing the first solid-state polyelectrolyte bipolar membrane which has the proton conductivity it is nonconducting from phosphoric-acid radical content resin and a reinforcement sheet applies, it is characterized by carrying out the polymerization of the phosphoric-acid radical content partial saturation monomer.

[0015] In the above-mentioned approach, whether the constituent containing a phosphoric-acid radical content partial saturation monomer and a photopolymerization initiator is infiltrated into a reinforcement sheet, and after applying, it is desirable by inserting a reinforcement sheet into the support substrate of diactinism, and irradiating ultraviolet rays to carry out the polymerization of the phosphoric-acid radical content partial saturation monomer.

[0016] Second solid-state polyelectrolyte bipolar membrane which has the proton conductivity of this invention is characterized by consisting of a phosphoric-acid radical / sulfonic group content resin, and a reinforcement sheet. As for a phosphoric-acid radical / sulfonic group content resin, it is desirable that it is the copolymer of the phosphoric-acid radical content partial saturation monomer which has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular, and the sulfonic group content partial saturation monomer which has one or more sulfonic groups and one or more ethylene nature unsaturated bonds in intramolecular.

[0017] The approach of manufacturing the second solid-state polyelectrolyte bipolar membrane which has the proton conductivity it is nonconducting from a phosphoric-acid radical / sulfonic group content resin, and a reinforcement sheet The phosphoric-acid radical content partial saturation monomer which has one or more phosphoric-acid radicals and one or more ethylene nature unsaturated bonds in intramolecular, The constituent containing the sulfonic group content partial saturation monomer which has one or more sulfonic groups and one or more ethylene nature unsaturated bonds in intramolecular Whether a reinforcement sheet is infiltrated and after applying, it is characterized by copolymerizing a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer.

[0018] In the above-mentioned approach, whether the constituent containing a phosphoric-acid radical content partial saturation monomer, a sulfonic group content partial saturation monomer, and a photopolymerization initiator is infiltrated into a reinforcement sheet, and after applying, it is desirable by inserting a reinforcement sheet into the support substrate of diactinism, and irradiating ultraviolet rays to copolymerize a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer.

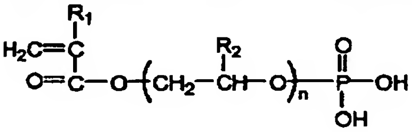
[0019] While the first [of this invention] and second solid-state polyelectrolyte bipolar membrane is all 30-80-degree C temperature requirements in a moisture state and shows the high conductivity of the range of 10-5-10-2 Scm-1, weight reduction initiation temperature has the outstanding thermal resistance of 200 degrees C or more, and does not cause change of appearances, such as telescopic motion, curvature, and interlaminar peeling, in the range of 30-100 degrees C, but shows the outstanding dimensional stability. The conductive temperature dependence of especially the solid-state polyelectrolyte bipolar membrane containing a phosphoric-acid radical / sulfonic group content resin is notably low, and the temperature requirement which is 30-80 degrees C shows the high conductivity of the range of 10-3-10-2 Scm-1.

[0020] Moreover, in preparing the proton conductivity polyelectrolyte film, the polyelectrolyte prepared beforehand is dissolved in an organic solvent, and by the manufacture approach of this invention, ultraviolet rays are irradiated at a monomer constituent, and with a conventional method, the place which carries out cast film production, since copolymerization is carried out, it is released from a polymerization or the complicatedness which deals with an organic solvent.

[0021]

[Embodiment of the Invention] Hereafter, the proton conductivity solid-state polyelectrolyte (compound) film containing the phosphoric-acid radical content resin of this invention, or a phosphoric-acid radical / sulfonic group content resin and those manufacture approaches are explained to a detail.

[I] the phosphoric-acid radical content resin, and the phosphoric-acid radical / sulfonic group content resin used for phosphoric-acid [redacted]al content resin, and a phosphoric-ac[redacted]dical / sulfonic group content resin this invention -- following [redacted]eral formula (A): -- [Formula 8]



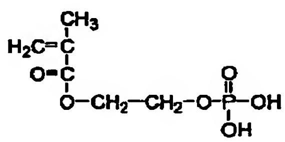
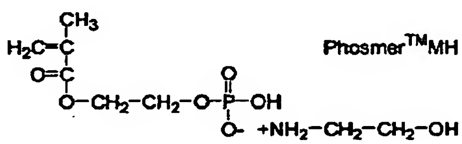
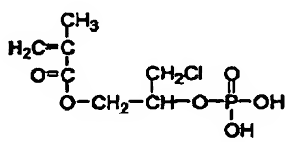
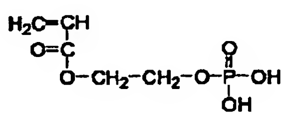
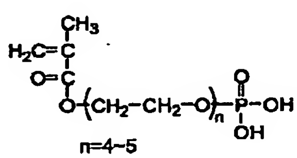
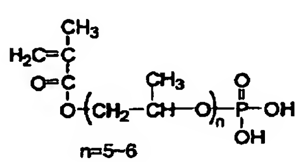
… (A)

(-- however, R1 is hydrogen or an alkyl group, R2 is an alkyl group which is not permuted [hydrogen, a permutation or], and n is the integer of 1-6.) -- the phosphoric-acid radical content partial saturation monomer expressed -- an indispensable component -- carrying out -- a polymerization -- or it copolymerizes. R1 is H or CH3, and, as for R2, it is desirable that they are H, CH3, or CH2Cl. The above-mentioned phosphoric-acid radical content partial saturation monomer may be copolymerized with this and other partial saturation monomers which may be copolymerized.

[0022] (1) The structure expression of the monomer which can be used suitable for this invention among the phosphoric-acid radical content partial saturation monomers expressed by the phosphoric-acid radical content partial saturation monomer general formula (A) is shown in Table 1, and the physical properties of these monomers are shown in Table 2. these monomers -- uni-chemical one -- Co., Ltd. -- from -- it is sold as a trade name PhosmerTM. However, the phosphoric-acid radical content partial saturation monomer which can be used for this invention is not limited to these.

[0023]

[Table 1]

名称	構造式	グレード名
アシッド・ホスホオキシエチルメタクリレート		Phosmer™M
メタクロイル・オキシエチルアシッドホスフェート・モノエタノールアミン塩		Phosmer™MH
3-クロロ-2-アシッド・ホスホオキシプロピルメタクリレート		Phosmer™CL
アシッド・ホスホオキシエチルアクリレート		Phosmer™A
アシッド・ホスホオキシポリオキシエチレングリコールモノメタクリレート		Phosmer™PE
アシッド・ホスホオキシポリオキシプロピレングリコールメタクリレート		Phosmer™PP

[0024]

[Table 2]

グレード (Phosmer™)		M	MH	CL	A	PE	PP
分子量(g)/ﾘﾝ酸当量(g)		210	271	258.5	196	333	440
比重 (at 20℃)		1.392	1.302	1.453	1.468	1.248	1.157
屈折率 (nd at 20 °C)		1.4562	1.4815	1.4785	1.4664	1.4696	1.4577
粘度 (poise at 20 °C) Brookfield型粘度計 (ﾛｰﾀNo.) により測定		80 (No. 1)	800 (No. 2)	700 (No. 2)	320 (No. 2)	25 (No. 1)	55 (No. 2)
酸化	理論値	533.3	206.6	433.3	571.4	—	—
	実測値	500以下	196	410以下	—	320	255
製品のpH		—	9.4	—	—	—	—
水溶性	(wt % at 20℃)	4.1	4.3	1.3	9.4	—	—
	(wt % at 25℃)	—	—	—	—	4.0	3.2
単量体が可溶な溶媒		有機酸, ｹﾄﾝ, ｱﾙｺｰﾙ	2-ﾋﾄﾞﾛｷｼｴﾁﾙﾒﾀｸﾘﾚｰﾄ, ﾒﾀﾉｰﾙ, ｴﾀﾉｰﾙ, ｲｿﾌﾟﾛﾋﾟﾙｱﾙｺｰﾙ, ｱｸﾘﾙ酸, 酢酸	有機酸, ｹﾄﾝ, ｱﾙｺｰﾙ	同左	同左	ﾍﾞﾝｾﾞﾝ, ﾄﾙｴﾝ, ｷｼﾚﾝ

[0025] The phosphoric-acid radical content partial saturation monomer of a general formula (A) may be used independently, and may use two or more sorts together.
[0026] (2) Other partial saturation monomer above-mentioned phosphoric-acid radical content partial saturation monomers which may be copolymerized, and the partial saturation monomer which may be copolymerized can be divided roughly into the following two groups (2-1) and (2-2).
[0027] (2-1) The partial saturation monomer containing the partial saturation monomer acid radical containing an acid radical is a compound which has at least one acid radical and at least one ethylene nature unsaturated bond in intramolecular. A sulfonic group, a carboxylic-acid radical, etc. are mentioned as an acid radical. Among these, a sulfonic group content partial saturation monomer is desirable, and a phosphoric-acid radical / sulfonic group content resin is obtained by copolymerization of a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer. Its conductive temperature dependence is notably low while the solid-state polyelectrolyte (compound) film containing a phosphoric-acid radical / sulfonic group content resin has the further excellent conductivity.
[0028] As an example of a sulfonic group content partial saturation monomer, an allyl compound sulfonic acid, a meta-allyl compound sulfonic acid, a vinyl sulfonic acid, p-styrene sulfonic acid, a butyl acrylate (meta)-4-sulfonic acid, an AKURIRO (meta) oxybenzene sulfonic acid, t-butyl acrylamide sulfonic acid, 2-acrylic-2-acrylamido-2-methyl propane sulfonic acid, etc. are mentioned. p-styrene sulfonic acid is desirable especially. However, since the allyl group starts degradative chaintransfer, as for an allyl compound sulfonic acid and a meta-allyl compound sulfonic acid, it is desirable to make the amount used into less than 65 % of the weight. These sulfonic group content partial saturation monomers may be independent, and may use two or more sorts together. As an example of a carboxylic-acid radical content partial saturation monomer, an acrylic acid (meta), a crotonic acid, a maleic acid, a fumaric acid, an itaconic acid, a maleic-acid anhydride, etc. are mentioned. These carboxylic-acid radical content partial saturation monomers may be independent, and may use two or more sorts together.
[0029] (2-2) Partial saturation monomer which does not contain an acid radical (2-1) Although it is except having indicated and not a gas but all the partial saturation monomers that have one or more ethylene nature unsaturated bonds in intramolecular are contained in this partial saturation monomer in ordinary temperature, acrylonitrile, acrylic ester (meta), and the styrene that is not permuted [a permutation or] are suitable especially (meta). It is desirable to use ethylene GURIKORUJI (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, hexamethylene JIORUJI (meta) acrylate, a divinylbenzene, etc. which contain two or more ethylene nature unsaturated bonds in 1 intramolecular in order to improve the chemical resistance of the solid-state polyelectrolyte (compound) film.
[0030] (3) Weight ratio phosphoric-acid radical content partial saturation monomer of each partial saturation monomer (1) Other partial saturation monomers (2) Weight ratio (1) / (2) Although it is the range

of 100 / 0 – 20/80, it is (1)/(2) preferably. = it is 80 / 20 – 50/50. Moreover, other partial saturation monomers (2) Partial saturation monomer which contains an acid radical inside (2-1) The other partial saturation monomer (2-2) A weight ratio brings the plus effectiveness to proton conductivity (2-1). It is desirable to consider as the range of (2-1) / (2-2) = 100 / 0 – 50/50 so that it may become dominant. therefore, the case where a sulfonic group content partial saturation monomer is used as a partial saturation monomer (2-1) containing especially an acid radical -- the weight ratio of a phosphoric-acid radical content partial saturation monomer / sulfonic group content partial saturation monomer -- 100 / 0 – 20/80 -- it is 80 / 20 – 50/50 preferably, and the weight ratios of an acid radical content partial saturation monomer besides sulfonic group content partial saturation monomer/are 100 / 0 – 50/50.

[0031] [II] As a photopolymerization initiator added to a monomer constituent by photopolymerization initiator this invention (1) -- R-(CO) x-R' (R, R' = hydrogen, or a hydrocarbon group --) the contiguity poly ketone compounds (for example, diacetyl --) expressed by x = 2-3 (2), such as dibenzyl a-carbonyl alcohols expressed by R-CO-CHOH-R' (R and R' = hydrogen or hydrocarbon group) (for example, benzoin etc.), (3) Acyloin ether expressed by R-CH(OR")-CO-R' (R, R', R"= hydrocarbon group) (for example, benzoin methyl ether etc.), (4) a-permutation acyloins (for example, a-alkyl benzoin etc.) expressed by Ar-CR(OH)-CO-Ar (Ar = aryl group and R = hydrocarbon group) and (5) There are polykaryotic quinones (for example, 9, 10-Anthraquinone, etc.). These photopolymerization initiators are independent respectively, or can be used together and used.

[0032] the amount of the photopolymerization initiator used -- the sum total weight of a partial saturation monomer -- receiving -- 0.5 – 5% of the weight of the range -- it is 1 – 3% of the weight of the range preferably. If it is less than 0.5 % of the weight, since a polymerization or copolymerization will not be completed in predetermined UV irradiation time amount but an unreacted monomer will remain, it is not desirable. Moreover, the polymerization degree of the resin obtained with super-** 5% of the weight is too low, and since the amount of the photopolymerization initiator used is in the inclination which resin colors, it is not desirable.

[0033] By this invention, the dissolution into the monomer mixture of a photopolymerization initiator is made easy, the viscosity of a partial saturation monomer is lowered and it makes it easy to sink in to a reinforcement sheet, and the coating weight to a reinforcement sheet is made to decrease, and low boilers, such as a methanol and an acetone, may be added as a diluent for the purpose, such as making thin thickness of the solid-state polyelectrolyte (compound) film.

[0034] [III] The reinforcement sheet used for reinforcement sheet this invention can be divided roughly into the three following groups.

(1) The textile fabrics which consist of the sheet glass fiber which consists of an inorganic fiber, an alumina fiber, rock wool fiber, slag fiber, etc., a nonwoven fabric, paper, etc. are mentioned. the basis weight of the sheet which consists of an inorganic fiber -- 10 – 60 mg/cm2 -- desirable -- 10 – 40 mg/cm2 -- it is -- thickness -- 1-60 mum -- desirable -- 5-40 It is the range of mum.

[0035] (2) The textile fabrics which consist of the sheet nylon fiber which consists of organic fiber, polyester fiber, an acrylic fiber, an aramid fiber, etc., a nonwoven fabric, paper, etc. are mentioned. However, since the temperature of the solid-state polyelectrolyte (compound) film may rise to about 100 degrees C at the time of UV irradiation, it is required to have sufficient thermal resistance to bear it. The basis weight and thickness of a sheet it is thin from organic fiber are the same as the case of (1). However, when the monomer constituent sunk in or applied contains the partial saturation monomer which has strong acid radicals, such as a sulfonic group, since the textile fabrics which consist of nylon fiber, a nonwoven fabric, paper, etc. have weak acid resistance, they are unsuitable.

[0036] (3) As a resin film which sinks in or applies a resin film monomer constituent, films, such as polyethylene resin, polypropylene resin, Pori 3-methyl pentene resin, nylon 6 resin, polyester resin, thermoplastic polyurethane, polysulfone resin, polyether sulphone resin, polyether ether ketone resin, aramid resin, polyimide resin, and fluorine system resin, are desirable. Although a fine porosity film or a nonporous film is sufficient as a resin film, the viewpoint of the impregnating ability of a monomer constituent to the former is desirable. However, when the monomer constituent to infiltrate contains the partial saturation monomer which has strong acid radicals, such as a sulfonic group, since acid resistance of a nylon film is not strong, it is unsuitable.

[0037] In the case of a fine porosity film, the smallest possible one of the aperture of a fine hole is desirable, and it is desirable that it is especially a diameter of submicron one. Moreover, the larger possible one of the hole density of the whole fine porosity film is desirable, and it is especially desirable that it is 40 – 50% (opposite surface area). The thickness of a resin film is 1-40. mum is desirable and it is 5-25. The range of mum is more desirable.

[0038] Although it changes greatly with absorptivity of a monomer constituent if it puts in another way, as for the weight ratio of a reinforcement sheet / monomer constituent, generally, it is [the weight ratio of a reinforcement sheet and a monomer constituent] desirable the compatibility over the monomer constituent of a reinforcement sheet and that it is the range of 1 / 20 – 1/2.

[0039] [IV] After casting the constituent containing both the partial saturation monomer and a photopolymerization initiator for a shaping die in the case of the solid-state polyelectrolyte film which consists of a manufacture approach phosphoric-acid radical content partial saturation monomer of the solid-state polyelectrolyte (compound) film, and a sulfonic group content partial saturation monomer and covering with a diactinism plate, it can manufacture by irradiating ultraviolet rays and carrying out copolymerization of both the partial saturation monomer.

[0040] Moreover, whether in the case of the solid-state polyelectrolyte bipolar membrane which consists of a phosphoric-acid radical content partial saturation monomer (or a phosphoric-acid radical content partial saturation monomer and a sulfonic group content partial saturation monomer) and a reinforcement sheet, the constituent containing a partial saturation monomer and a photopolymerization initiator is infiltrated into a reinforcement sheet, and after applying, it can manufacture by inserting a reinforcement sheet into the support substrate of diactinism, irradiating ultraviolet rays, and photopolymerizing a partial saturation monomer.

[0041] It does not paste up with the solid-state polyelectrolyte obtained by carrying out the polymerization of having the thermal resistance which bears the temperature up at the time of the polymerization by ultraviolet-rays permeability being not only high but UV irradiation, a partial saturation monomer constituent, and this, but two support substrates which sandwich this in carrying out the UV irradiation polymerization of the reinforcement sheet which sank in the partial saturation monomer constituent need for detachability to be good.

[0042] Usually, although the glass plate to be used is very good about ultraviolet-rays permeability and thermal resistance, since it sticks with the solid-state polyelectrolyte obtained by the polymerization or copolymerization of a partial saturation monomer used for this invention, it is desirable to use it, after applying the remover of a silicone system or a fluorine system to the front face of a glass plate beforehand or sticking the thin bright film of a fluororesin system.

[0043] The resin plate which has the thermal resistance of 100 degrees C or more with sufficient ultraviolet-rays permeability, such as Pori 3-methyl pentene [besides fluorine system resin, such as polyperfluoro vinyl ether resin (PFA) and polyvinylidene fluoride resin (PVDF),] resin and polypropylene resin, in addition to a glass plate can be used.

[0044] In performing UV irradiation on both sides of whether it covers with a diactinism plate and UV irradiation is performed or a partial saturation monomer constituent is infiltrated, and the applied reinforcement sheet between two support substrates, after casting a partial saturation monomer constituent, it is necessary to press out air and an excessive partial saturation monomer constituent out of a system. For example, when using a reinforcement sheet, it is desirable to perform UV irradiation, keeping it level in the condition of having stopped by the clip or the clamp, having put the pressure equally between two support substrates, as shown in drawing 1 . the UV irradiation reinforcement at the time of photopolymerization -- 5 - 50 mW/cm2 -- it considers as 10 - 25 mW/cm2 preferably.

[0045] the thickness of the solid-state polyelectrolyte (compound) film -- 300 below mum -- desirable -- 10-100 mum -- more -- desirable -- 10-30 It is referred to as mum.

[Translation done.]

EXAMPLE

[Example] Although the following examples explain this invention to a detail further, this invention is not limited to these.
[0047] After adding the methanol to the partial saturation monomer constituent shown in one to examples 1-16 and example of comparison 4 table 3 as a diluent and adjusting viscosity to it, 2% of the weight of the IRUGA cure 651 (2 and 2-dimethoxy -1, 2-bibenzyl-1-ON) and 1% of the weight of the IRUGA cure 500 (1-hydroxy cyclohexyl phenyl ketone + benzophenone) were dissolved as a photopolymerization initiator, having used the whole partial saturation monomer as 100 % of the weight. After adopting various kinds of nonwoven fabrics or papers as a reinforcement sheet and infiltrating a partial saturation monomer constituent into a reinforcement sheet, as shown in drawing 1 and drawing 2 , it is partial saturation monomer constituent sinking-in reinforcement sheet **** between two glass plates which applied the silicone remover. Using the high pressure mercury vapor lamp (the toss cure 400 by Toshiba Electric Equipment Corp., and HC-0411 mold), the predetermined time exposure of the ultraviolet rays of 20 mW/cm2 was carried out, photopolymerization of the partial saturation monomer constituent was carried out to the partial saturation monomer constituent sinking-in reinforcement sheet, and solid-state polyelectrolyte bipolar membrane was produced. The class of a partial saturation monomer constituent and reinforcement sheet and a basis weight, UV irradiation time amount, and the description of bipolar membrane are shown in Table 3.
[0048]
[Table 3]

例 No.		実施例 1			実施例 2			実施例 3	
不飽和単量体組成物 (wt. %)	Phosmer M	50			—			50	
	Phosmer PP	50			95			50	
	PSSA(1)	—			—			—	
	HDDA(2)	—			5			—	
希釈剤 MeOH (wt. %)		0	50	75	0	50	75	50	75
補強材シート	種類	GF 不織布 GHN-30CGL(3)			GF 不織布 GHN-30CGL			GF 不織布 GMC-050E(4)	
	坪量(mg/cm²)	30			30			50	
照射時間 [表＋裏 (sec)]		40 + 40			40 + 40			40 + 40	
複合膜	樹脂／補強材シート(10)	9.6	7.5	4.7	8.5	6.1	4.2	7.2	4.0
	平滑性	良好			良好			良好	
	ピンホール	ナシ			ナシ			ナシ	
	厚さ(μm)	170	140	110	160	130	110	170	120
	導電率測定の有無	No			No			Yes	No

例 No.		実施例 4		実施例 5	実施例 6
不飽和単量体組成物 (wt. %)	Phosmer M	—		50	—
	Phosmer PP	95		50	95
	PSSA[1]	—		—	—
	HDDA[2]	5		—	5
希釈剤 MeOH (wt. %)		50	75	75	50
補強材シート	種類	GF 不織布 GMC-050E		GF 紙[5]	GF 紙
	坪量(mg/cm²)	50		40	40
照射時間 [表+裏 (sec)]		40 + 40		40 + 40	40 + 40
複合膜	樹脂／補強材シート[10]	6.0	5.0	4.5	5.3
	平滑性	良好		良好	良好
	ピンホール	ナシ		ナシ	ナシ
	厚さ(μm)	160	100	90	87
	導電率測定の有無	Yes	No	No	No

[0049] Table 3 continuation

例 No.		実施例 7	実施例 8	実施例 9
不飽和単量体組成物 (wt. %)	Phosmer M	50	—	50
	Phosmer PP	50	95	50
	PSSA[1]	—	—	—
	HDDA[2]	—	5	—
希釈剤 MeOH (wt. %)		75	50	75
補強材シート	種類	PAN 紙[6]	PAN 紙	アラミド不織布 XL-1040[7]
	坪量(mg/cm²)	38	38	40
照射時間 [表+裏 (sec)]		40 + 40	40 + 40	120 + 120
複合膜	樹脂／補強材シート[10]	3.8	5.0	13.3
	平滑性	良好	良好	良好
	ピンホール	ナシ	ナシ	ナシ
	厚さ(μm)	75	70	200
	導電率測定の有無	Yes	Yes	Yes

[0050] Table 3 continuation

例 No.		実施例 10	実施例 11	実施例 12
不飽和単量体組成物 (wt. %)	Phosmer M	—	50	—
	Phosmer PP	95	50	95
	PSSA(1)	—	—	—
	HDDA(2)	5	—	5
希釈剤 MeOH (wt. %)		50	75	50
補強材シート	種類	アラミド不織布 XL-1040	アラミド紙(8)	アラミド紙
	坪量(mg/cm²)	40	35	35
照射時間［表＋裏 (sec)］		120 + 120	120 + 120	120 + 120
複合膜	樹脂／補強材シート(10)	10.1	5.6	4.7
	平滑性	良好	良好	良好
	ピンホール	ナシ	ナシ	ナシ
	厚さ(μm)	190	45	38
	導電率測定の有無	Yes	Yes	Yes

[0051] Table 3 continuation

例 No.		実施例 13	実施例 14	実施例 15
不飽和単量体組成物 (wt. %)	Phosmer M	50	—	50
	Phosmer PP	50	95	—
	PSSA(1)	—	—	50
	HDDA(2)	—	5	—
希釈剤 MeOH (wt. %)		50	50	70
補強材シート	種類	ハイポア 6022(9)	ハイポア 6022	GF 不織布 GHN-30CGL
	坪量(mg/cm²)	25	25	30
照射時間［表＋裏 (sec)］		40 + 40	40 + 40	60 + 60
複合膜	樹脂／補強材シート(10)	3.1	2.7	2.3
	平滑性	良好	良好	良好
	ピンホール	ナシ	ナシ	ナシ
	厚さ(μm)	37	20	104
	導電率測定の有無	No	No	Yes

[0052] Table 3 continuation

例 No.		実施例 16	比較例 1	比較例 2
不飽和単量体組成物 (wt. %)	Phosmer M	50	50	—
	Phosmer PP	—	50	95
	PSSA(1)	50	—	—
	HDDA(2)	—	—	5
希釈剤 MeOH (wt. %)		70	50	50
補強材シート	種類	ナイロンネット	—	—
	坪量(mg/cm²)	50	—	—
照射時間 [表＋裏 (sec)]		60 + 60	40 + 40	40 + 40
複合膜	樹脂／補強材シート(10)	0.8	—	—
	平滑性	良好	良好	良好
	ピンホール	ナシ	ナシ	ナシ
	厚さ(μm)	約 100	約 30	約 20
	導電率測定の有無	Yes	No	No

[0053] Table 3 continuation

例 No.		比較例 3	比較例 4
不飽和単量体組成物 (wt. %)	Phosmer M	—	—
	Phosmer PP	—	—
	PSSA(1)	100	100
	HDDA(2)	—	—
希釈剤 MeOH (wt. %)		82	82
補強材シート	種類	GF 不織布 GHN-30CGL	ナイロンネット
	坪量(mg/cm²)	30	50
照射時間 [表＋裏 (sec)]		60 + 60	60 + 60
複合膜	樹脂／補強材シート(10)	1.4	0.3
	平滑性	良好	良好
	ピンホール	ナシ	ナシ
	厚さ(μm)	52	100
	導電率測定の有無	Yes	Yes

[0054] Table 3 continuation

Note : (1) PSSA: p-styrene sulfonic acid (2) HDDA: Hexamethylene diol diacrylate (3) GF (glass fiber) nonwoven fabric GHN-30CGL (commercial item by Oji Paper Co., Ltd.)
(4) GF (glass fiber) nonwoven fabric GMC-050E (commercial item by Oji Paper Co., Ltd.)
(5) GF (glass fiber) paper (prototype by Awa Paper Manufacturing Co., Ltd.)
(6) PAN (polyacrylonitrile) paper (prototype by Awa Paper Manufacturing Co., Ltd.)
(7) Aramid nonwoven fabric XL-1040 (prototype by Japan Vilene Co., Ltd.)
(8) Aramid paper (prototype by Awa Paper Manufacturing Co., Ltd.)
(9) PE (polyethylene) fine porosity film High pore TM 6022 (Asahi Chemical Industry Co., Ltd. make)
(10) The weight ratio of resin / reinforcing materials sheet.

[0055] About the typical solid-state polyelectrolyte bipolar membrane of an example and the example of a

comparison, conductivity was measured at 90% of relative humidity, and 30-80 degrees C of temperature requirements. A result is shown in drawing 3 - drawing 5 .

[0056] If the approach of this invention is followed, even if it will use which reinforcement sheet from the result shown in drawing 3 - drawing 5 , a front face is smooth, and it turns out that solid-state polyelectrolyte bipolar membrane without a pinhole can be made. In addition, by using a diluent, the amount of resin adhering to a reinforcement sheet was able to be made into less than [1/several]. The thickness of the solid-state polyelectrolyte bipolar membrane of an example is 20-200. Although it is the range of mum, it can consider as desired thickness the basis weight of a reinforcement sheet, the compatibility of a reinforcement sheet and a partial saturation monomer constituent, the adhesion rate of resin, and by adjusting suitably the coating weight of a monomer constituent, and the pressure which presses it out, if it puts in another way.

[0057] It turns out that it is in a level good as a polyelectrolyte which the conductivity of the solid-state polyelectrolyte bipolar membrane of this invention is the order of 10-5-10-2 Scm-1, and makes a phosphoric-acid radical a functional group from the result shown in drawing 3 - drawing 5 . The conductive temperature dependence of especially the solid-state polyelectrolyte bipolar membrane (examples 15 and 16) containing the phosphoric-acid radical / sulfonic group content resin which consists of a copolymer of a phosphoric-acid radical content partial saturation monomer and p-styrene sulfonic acid was remarkably low, and the temperature requirement which is 30-80 degrees C showed 10-3-10-2 Scm-1 and high conductivity. On the other hand, since the solid-state polyelectrolyte bipolar membrane of the examples 3 and 4 of a comparison uses the homopolymer of p-styrene sulfonic acid, compared with the solid-state polyelectrolyte bipolar membrane of examples 15 and 16, its conductivity is low, and its conductive temperature dependence is high.

[0058] Although the above example showed the experimental result of the solid-state polyelectrolyte bipolar membrane which has a reinforcement sheet, it is clear to have the electrolyte property same as the solid-state polyelectrolyte film which does not have a reinforcement sheet. Therefore, the solid-state polyelectrolyte film which does not have a reinforcement sheet can be suitably used for the application as which a high mechanical strength is not required.

[Translation done.]

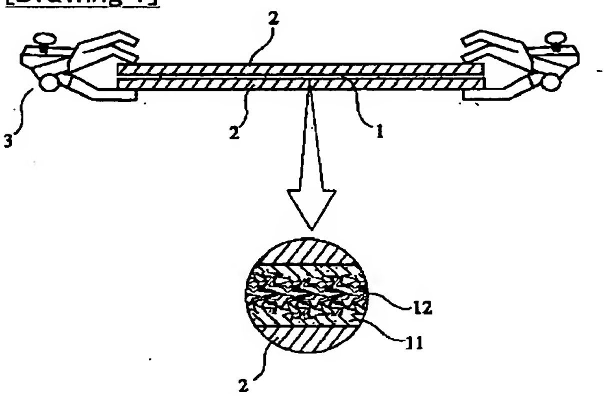
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the partial cross-section side elevation showing the condition of having pinched solid-state polyelectrolyte bipolar membrane between two glass plates.
[Drawing 2] It is the top view showing the condition of having pinched solid-state polyelectrolyte bipolar membrane between two glass plates.
[Drawing 3] (a) is a graph which shows the relation between temperature T (degree C) and conductivity log (sigma/Scm -1) about the solid-state polyelectrolyte bipolar membrane of examples 3 and 4, and (b) is a graph which shows the relation between temperature T (degree C) and conductivity log (sigma/Scm -1) about the solid-state polyelectrolyte bipolar membrane of examples 7 and 8.
[Drawing 4] (a) is a graph which shows the relation between temperature T (degree C) and conductivity log (sigma/Scm -1) about the solid-state polyelectrolyte bipolar membrane of examples 9 and 10, and (b) is a graph which shows the relation between temperature T (degree C) and conductivity log (sigma/Scm -1) about the solid-state polyelectrolyte bipolar membrane of examples 11 and 12.
[Drawing 5] (a) is a graph which shows the relation between temperature T (degree C) and conductivity log (sigma/Scm -1) about the solid-state polyelectrolyte bipolar membrane of an example 15 and the example 3 of a comparison, and (b) is a graph which shows the relation between temperature T (degree C) and conductivity log (sigma/Scm -1) about the solid-state polyelectrolyte bipolar membrane of an example 16 and the example 4 of a comparison.

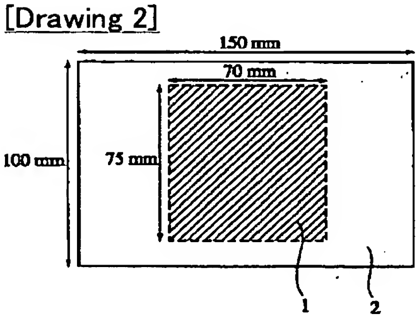
[Translation done.]

DRAWINGS

[Drawing 1]

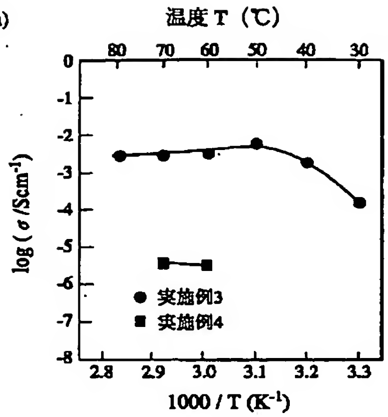


[Drawing 2]

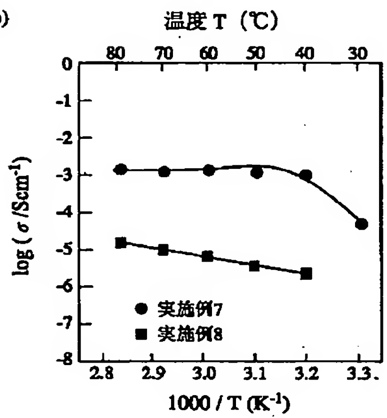


[Drawing 3]

(a)

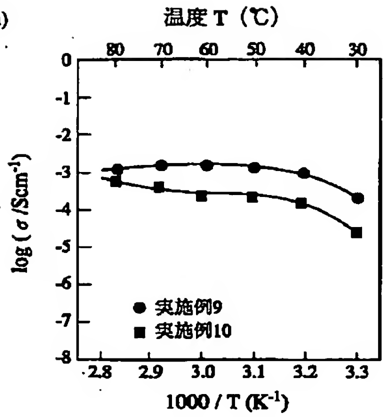

温度 T（℃）
80 70 60 50 40 30
log (σ /Scm-1)
0 -1 -2 -3 -4 -5 -6 -7 -8
● 実施例3
■ 実施例4
2.8 2.9 3.0 3.1 3.2 3.3
1000 / T (K-1)

(b)

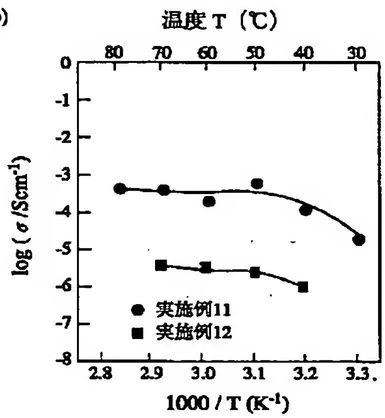

温度 T（℃）
80 70 60 50 40 30
log (σ /Scm-1)
0 -1 -2 -3 -4 -5 -6 -7 -8
● 実施例7
■ 実施例8
2.8 2.9 3.0 3.1 3.2 3.3
1000 / T (K-1)

[Drawing 4]

(a)

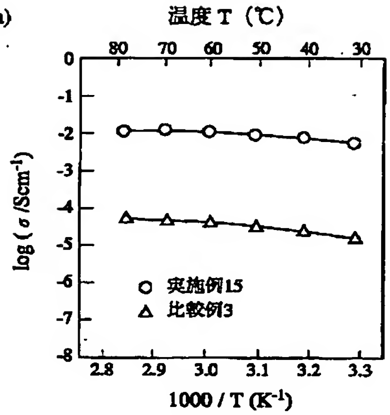

温度 T（℃）
80
70
60
50
40
30
0
-1
-2
-3
-4
-5
-6
-7
-8
log (σ /Scm-1)
● 実施例9
■ 実施例10
2.8
2.9
3.0
3.1
3.2
3.3
1000 / T (K-1)

(b)

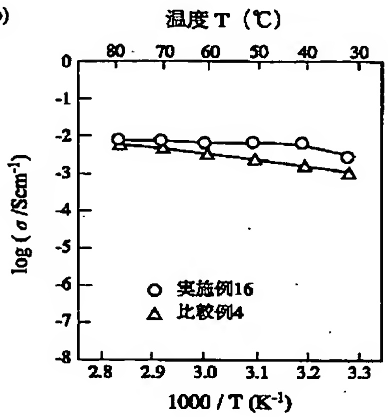

温度 T（℃）
80
70
60
50
40
30
0
-1
-2
-3
-4
-5
-6
-7
-8
log (σ /Scm-1)
● 実施例11
■ 実施例12
2.8
2.9
3.0
3.1
3.2
3.3
1000 / T (K-1)

[Drawing 5]

(a)



(b)



[Translation done.]